OPTICAL LIMITING WITH NANOHYBRID COMPOSITES

FIELD OF INVENTION

The invention relates to an optical limiter, and in particular, to optical limiter with nanohybrid composites that are effective towards femtosecond laser pulses.

BACKGROUND TO THE INVENTION

The following discussion of the background to the invention is intended to facilitate an understanding of the present invention. However, it should be appreciated that the discussion is not an acknowledgment or admission that any of the material referred to was published, known or part of the common general knowledge in any jurisdiction as at the priority date of the application.

As more and more powerful pulsed lasers become widely available, there is a growing need for the protection of optical sensors or human eyes from intense laser irradiation. There have been significant research efforts and advances in the field of nonlinear optics, whereby the light absorption and/or light scattering of a material increase with the energy of incident laser pulses. The nonlinear processes in organic molecules, polymers and nanomaterials have been extensively investigated, including two-photon absorption, excited-state absorption, and light-energy-dependent scattering (or nonlinear scattering). However, the lack of strong performers in conventional nonlinear materials has hindered practical applications.

A desirable optical limiter should be highly transparent at low light irradiance, but opaque under high laser irradiation, and should exhibit fast switching between these two states. It also needs to be functional in broad temporal and spectral ranges with a high damage threshold. Effective optical limiting of nanosecond laser pulses is achievable by utilizing the excited-state absorption in fullerenes and phthalocyanine complexes, and the nonlinear scattering in carbon nanotubes, nanoparticles and metallic nanowires. Excited-state absorbers have been proven to be one of the best limiters, but they perform poorly in response to femtosecond laser pulses. On the other hand, optical limiters based on nonlinear scattering

provide broadband limiting because the origin of the creation of new scattering centers is thermal in nature: self thermal expansion due to absorption of intense laser energy and formation of ionized microplasmas and/or solvent microbubbles. Such limiters, however, are known to be less effective towards femtosecond laser pulses.

To regulate intense femtosecond laser pulses, two-photon absorption (TPA) in semiconductor quantum dots and organic molecules has been proposed and investigated. The best TPA cross-sections are found to be 10^3–10^6 Goeppert-Mayer units (1 GM = 10^{-50} cm^4 s per photon). Such two-photon absorbers typically exhibit poor performance towards nanosecond laser pulses because the intensities of nanosecond laser pulses are inadequate to induce significant TPA prior to laser-induced damage in the material.

There have been many attempts to enhance nanosecond optical limiting by blending two materials that are two-photon absorbers, excited-state absorbers or nonlinear scatterers. No study has been reported on enhancing femtosecond limiting performance.

It is desirable to provide an optical limiter that possesses the above properties.

SUMMARY OF THE INVENTION

Throughout this document, unless otherwise indicated to the contrary, the terms "comprising", "consisting of", and the like, are to be construed as non-exhaustive, or in other words, as meaning "including, but not limited to".

Herein we propose and demonstrate the engineering of nanohybrid composites for superior optical limiters on both femtosecond and nanosecond timescales. The nanohybrid composites consist of two components; one component is selected for its giant TPA, and the other is chosen for its metallic properties to reinforce nonlinear scattering induced by nanosecond laser pulses and to greatly enhance TPA through its surface plasmon. With this new approach, we have achieved a limiting threshold as low as approximately 0.01 J/cm^2 (or less than 10^2 GW/cm^2) for femtosecond laser pulses, and a limiting response as good as carbon nanotubes on the nanosecond time scale.

For example, components selected for its giant TPA include metal oxide(s) of at least one metal selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, In, Sn, Sb, Ta, W, Re, Os, Ir and Bi. And possible metals include Au and Ag. Further developments relating to the optical limiting materials are in the works, in particular, development of the material into a thin film/coating material. The nanohybrid composite optical limiters can be processed as thin films for applications in optical sensor and eye protection from laser beams.

Herein we present Fe_3O_4–Ag semiconductor-metal nanocomposites as a new type of broad temporal optical limiter. With these nanocomposites, we demonstrate that broad temporal optical limiting can be accomplished with low limiting threshold. Due to the presence of Ag nanoparticles, nonlinear scattering gives rise to enhanced optical limiting responses to 532-nm nanosecond laser pulses, with a limiting threshold comparable to carbon nanotubes. As exposed to 780-nm femtosecond laser pulses, the largest value (approximately 10^{-44} cm^4 s photon^{-1} or 10^6 GM) for two-photon absorption cross-sections reported to date results in superior limiting responses with a limiting threshold as low as 0.04 J/cm^2 or 100 GW/cm^2. The limiting threshold can be further reduced by increasing Ag particle size through plasmon enhancement or taking advantage of self-defocusing.

BRIEF DESCRIPTION OF THE DRAWINGS

In the figures, which illustrate, by way of example only, embodiments of the present invention,

FIG. 1 shows (**A**) low-resolution and (**B**) high-resolution TEM images of Fe_3O_4–Ag; (**C**) schematic of a Fe_3O_4–Ag nanohybrid composite with a capping layer.

Fig. 2 shows (**a**) absorption spectra of Fe_3O_4–Ag heterodimers (red) and Fe_3O_4 nanocubes (green) in toluene. The difference between the two spectra is shown by the black line. The inset displays the size distributions of Fe_3O_4 nanocubes and Ag nanoparticles, (**b**) powder XRD pattern of Fe_3O_4–Ag heterodimers.

Fig. 3 shows fluence-dependent transmittance measured for toluene solution of (▪) Fe_3O_4, nanocubes, (●) Fe_3O_4–Ag (7 nm) heterodimers and (▲) Fe_3O_4–Ag (10

nm) heterodimers, and (•) carbon nanotubes in water. (▼) Data were measured from Fe_3O_4–Ag (10 nm) heterodimers with an aperture of 90% transmittance placing in front of the transmission detector.

Fig. 4 shows (**a**) open-aperture Z-scans (open circles) with theoretical fits (solid lines). The inset shows the dependence of effective TPA coefficients on input irradiance. (**b**) Transient absorption measurements with two-exponential fittings (black solid lines). The measurements were conducted on the 1 mm-thick toluene solution of Fe_3O_4–Ag (7 nm) heterodimers with 780-nm and 330-fs laser pulses.

DETAILED DESCRIPTION

The invention relates to an optical limiter, and in particular, to optical limiter with nanohybrid composites that are effective towards femtosecond laser pulses.

Previous optical limiters were usually based on (i) nonlinear absorption (for high incident light intensity and short laser pulse duration: femtosecond), (ii) nonlinear scattering (relatively low incident light intensity, but high incident energy and long pulse duration: picosecond to nanosecond), or (iii) nonlinear refraction (requiring pinhole, can work from femtosecond to nanosecond). Very few materials operate with all three of these mechanisms at the same time. Herein we report the design and development of semiconductor–metal hybrid nanoparticles. For the semiconductor component, we have selected Fe_3O_4, which we have demonstrated to possess the largest two-photon-absorption and refraction cross-sections reported to date. For the metal component, we have chosen Ag, which possesses outstanding nonlinear scattering and surface plasmons. This semiconductor–metal hybrid nanoparticle system is not simply a uniform mixture of semiconductor nanoparticles and metal nanoparticles, but rather a heterodimer nanocomposite system. The surface plasmon of Ag nanoparticle is found to further enhance the two-photon absorption and refraction of the Fe_3O_4 component. This results in an optical limiter that possesses the largest two-photon absorption and refraction, as well as outstanding nonlinear scattering. The novel materials can provide for optical limiting from the femtosecond to nanosecond with an ultralow optical limiting threshold.

We selected Fe_3O_4 nanocrystals as a key component of the nanohybrid composite since Fe_3O_4 is well-known for its large TPA, and is expected to give rise to superior limiting performance when exposed to femtosecond laser pulses. Furthermore, a Fe_3O_4 nanocube is chosen because TPA theories on CdS nanocrystals conclude that the cubic shape should provide the largest the TPA cross-section, compared to spherical or cylinder shapes for a given volume. In addition, recent findings show that Fe_3O_4 nanocrystals are also an effective nonlinear scatterer. Silver nanoparticles are chosen as the metallic component for the nanohybrid composite due to its ease of synthesis with Fe_3O_4 nanocrystals, high chemical and thermal stability, as well as excellent limiting property under nanosecond laser excitation. The Fe_3O_4–Ag heterodimer exhibited unique synergistic features in its optical properties. In particular, the surface plasmon of Ag particles considerably enhanced the effective TPA on the femtosecond time scale, as elaborated below.

Material synthesis and characterizations

The Fe_3O_4 nanocubes were synthesized by thermal decomposition of iron oleate complex following published procedures known to person skilled in the art. The Fe_3O_4–Ag heterodimers were prepared by seeded growth using pre-synthesized Fe_3O_4 nanocubes as seeds. High-resolution transmission electron microscopy (TEM) was used to characterize the structure of the heterodimers. The Fe_3O_4 nanocubes and Ag nanoparticles were nearly monodispersed with a size dispersion of 20% or less, and with an average length and an average diameter of 13 nm and 7 nm, respectively (see **Figs. 1(A)**, **1(B)** and **2(a)** (inset)). The heterodimers were capped with an organic layer of oleic acid and oleylamine molecules, respectively (see **Fig. 1(C)**). The X-ray diffraction (XRD) pattern in **Fig. 2(b)** clearly illustrates the crystalline peaks associated with Fe_3O_4 phase and Ag phase.

Fig. 2(a) shows the comparison between the linear (or small-signal) absorption spectra of Fe_3O_4–Ag heterodimers and Fe_3O_4 nanocubes in toluene. In the spectral range from 200 to 1000 nm, the similarity between the two spectra suggested that the absorption was predominated by the Fe_3O_4 nanocubes. Shown by the black line in **Fig. 2(a)**, the slight difference between the two spectra reflected the

presence of the Ag nanoparticles, which manifested themselves by a surface plasmon resonance (SPR) at approximately 410 nm, in agreement with the Mie's theory for 7-nm Ag nanoparticles in toluene. The fundamental absorption band edge of the pure Fe_3O_4 nanocubes was uncertain due to the fact that a number of narrow *d-d* bands lie within the gap, some of which even extended to the infrared with a definite probability.

Optical limiting measurements

The nanosecond experiment was conducted with 7-ns, 532-nm and 10-Hz laser pulses, which were produced by a Q-switched and frequency-doubled Nd:YAG laser. The laser pulses were divided into two parts with a beam splitter; one part was taken as the reference, and the other part was focused onto the sample with a concave mirror (f = 25 cm). The beam radius at the focus was 35±4 μm. The incident and transmitted pulse energies were measured with two energy detectors (Laser Probe RjP-735) simultaneously. The single-walled carbon nanotubes suspended in water were measured under the same conditions as a reference. **Fig. 3(a)** shows that the limiting performance of the Fe_3O_4–Ag (7nm) solution was marginally better than that of the carbon nanotube suspension, which has been known as a benchmark optical limiter. The Fe_3O_4–Ag (7nm) heterodimers outperformed the Fe_3O_4 nanocubes in the context of limiting threshold, defined as the incident fluence at which the transmittance falls to 50% of the normalized linear transmittance. The limiting threshold of the heterodimer solution was approximately 2.5 J/cm^2, which was half of that of Fe_3O_4 solution, indicating that the optical limiting of nanosecond laser pulses benefitted from the presence of Ag nanoparticles. Our nonlinear scattering measurements (not shown here) also provided similar conclusions, and confirmed that the observed limiting property should be induced mainly by nonlinear scattering.

The femtosecond experiments were conducted with 330-fs (FWHM), 780-nm and 1-kHz laser pulses, which were generated by a Ti:Sapphire regenerative amplifier (Titan, Quantronix). The enhanced optical limiting of femtosecond laser pulses is illustrated in **Fig. 3(b)**. The limiting threshold of Fe_3O_4–Ag (7 nm) solution was approximately 0.04 J/cm^2 (or approximately 10^2 GW/cm^2), which is about one order of magnitude lower than that of Fe_3O_4 nanocubes, and two orders of

magnitude better than the reported value for iron oxide nanoparticles. The TPA and optical Kerr nonlinearity (n_2) could be determined unambiguously by conducting open-aperture and close-aperture Z-scans, respectively. Typical Z-scans on Fe_3O_4–Ag (7 nm) are depicted in **Fig. 4(a)**. By assuming spatially and temporally Gaussian profiles for the input laser pulses, Z-scans can be fit by solving the propagation equation of electric field envelope *E*:

$$\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial E}{\partial r}) - 2ik\frac{\partial E}{\partial z} - ik\alpha E + \frac{2k^2}{n_0}n_2|E^2|E = 0 \qquad (1)$$

where *k* is wave vector, $\alpha(I) = \alpha_0 + \alpha_2 I$ describes both one-photon and two-photon absorption, and *I* is the light irradiance.

From the best fits, we extracted the effective TPA coefficients (α_2) and plotted them as a function of the laser irradiance (see **Fig. 4(a)** inset). From the intercept, the intrinsic TPA coefficient was determined as α_2 = 0.040±0.005 cm/GW. The TPA cross-section (σ_2) was then derived as 1.3 × 10^7 GM from $\sigma_2 = (\hbar\omega)\alpha_2 / N$, where *N* was the heterodimer density (8 × 10^{13} cm^{-3}). This value was one order of magnitude greater than the largest value published for organic molecules and at least two orders of magnitude higher than the values reported for semiconductor quantum dots. The slope of the line was related to both excited-state absorption (ESA) cross-section and lifetime. At higher laser excitation, TPA and ESA could be effectively treated as a two-step three-photon absorption process, consistent with the previous findings.

Definite understanding of the two-photon transitions would require quantum chemical computations for excited states in the Fe_3O_4 nanocube. Such theoretical studies are difficult for transition metal species with an unfilled *d* electron shell. The enhancement in the measured TPA of Fe_3O_4–Ag heterodimers, however, was a consequence of the presence of surface plasmon resonance (SPR) in the Ag nanoparticle. The nonlinear absorption contribution from the same concentration of Ag nanoparticles in toluene is negligible within our experiment uncertainty. Recently, a 157-fold enhancement has been reported for the effective TPA cross-section of organic dye through an electric-field augmentation via the SPR of Au nanospheres. The SPR enhancement is related to the metal dielectric constant,

solvent dielectric constant, excitation wavelength and metal particle size. Herein we demonstrated that the σ_2 of Fe_3O_4 (13 nm) nanocubes could be tailored through altering the size of Ag nanospheres. As the Ag diameter was increased from 0 to 10 nm, the σ_2 was increased from 0.3×10^7 GM to 1.8×10^7 GM.

The enhanced σ_2 could greatly reduce the limiting threshold. **Fig. 3(b)** clearly demonstrates that the greater the size of the Ag nanoparticles, the lower was the limiting threshold. To further reduce the limiting threshold, one might take advantage of self-defocusing, originating from the enhanced optical-Kerr nonlinearity in the heterodimer. Our close-aperture Z-scans (not shown here) indicated that the optical Kerr nonlinearity was negative. Similarly, the measured nonlinear refractive cross-sections were found to increase with the Ag particle size (see **Table 1**), which was indicative of an enhancement by the presence of SPR in Ag particles. With an aperture of 90% transmittance placed in front of the transmission detector, the limiting threshold became as low as 0.01 J/cm^2 or 30 GW/cm^2 (see **Fig. 3(b)**).

Table 1. Effective nonlinear refractive and TPA cross-sections

Fe_3O_4 Length (nm)	Ag Diameter (nm)	σ_n (cm^5/GW)	σ_2 (GM)
13	0	-4.2×10^{-20}	0.3×10^7
13	3.5	-5.8×10^{-20}	0.9×10^7
13	7	-6.5×10^{-20}	1.3×10^7
13	10	-8.1×10^{-20}	1.8×10^7

*Experimental uncertainty: ±40%

This Ag size dependence could be quantitatively understood from the enhanced electric field in the Fe_3O_4 nanocube by the presence of Ag nanoparticle. We conducted the theoretical calculations based on the Discrete Dipole Approximation (DDA). In our calculation, the incident laser pulse was linearly polarized, and the influence of neighboring nanohybrid composites was ignored since the average center-to-center spacing between Ag particles was greater than

200 nm in the experiments. The complex refractive index used for toluene is: $n_{toluene}$ = 1.5, for Ag if n_{Ag} = 0.14+5.13i at a wavelength of 780 nm. The relative enhancement in the local electric field ($E_r = E/E_0$, where E and E_0 are the total local electric field and the incident light's electric field, respectively) of Ag particle at a plane containing the axes of light propagation and polarization can be obtained. Considering the randomness of orientation for the nanohybrid composites, we averaged the cube of the enhanced local electric field over all directions to obtain $<|E_r(R)|^3>$ at each distance (R) to the Ag sphere center. With such numeric results, the effective TPA cross-section of Fe_3O_4 nanocubes could be calculated using:

$$\sigma_{effective} = \frac{\int_{cubic} \sigma_{Fe_3O_4} \cdot < |E_r(R)|^3 > dv}{\int_{cubic} dv} \quad (2)$$

We define the enhancement factor as $\sigma_{effective} / \sigma_{Fe_3O_4}$. As shown in **Table 2**, the enhancement factors predicated by the above model were in agreement with the experimental data, within the experimental errors.

Table 2. Enhancement factor in TPA

Enhancement	Fe_3O_4–Ag (3.5 nm)	Fe_3O_4–Ag (7 nm)	Fe_3O_4–Ag (10 nm)
Experiment	3	4.3	6
Theory	2.3	7.2	11.7

*Experimental uncertainty: ±40%

The femtosecond time-resolved degenerate transient absorption experiments were conducted with the same laser system used in the aforementioned femtosecond measurements. After the spatial filter, the laser pulses were also divided into two parts; one part was used as the pump, and the other part was employed as the probe. The linear polarization of the probe pulse was adjusted to be perpendicular to that of the pump pulse with a polarizer and a quarter waveplate. The probe pulse energy was regulated to be less than 5% of the pump

pulse energy by utilizing neutral density filters. The experimental results are shown in **Fig. 4(b)**, where the decays were best fit with two exponentials. The fast time component was approximately 1 ps, while the slow time constant was in the range of 18–30 ps, depending on the pump pulse energy, which was different from the electron dynamics reported for iron oxide nanoparticles whereby the relaxation was independent of the pump intensity. With the Ag nanoparticle attachment, the difference should be anticipated as there existed an extra relaxation channel whereby some energy of the photoexcited carriers in the Fe_3O_4 nanocube was energy resonantly transferred to the metallic component, and subsequently dissipated through electron-electron, electron-phonon and phonon-phonon interactions.

We have demonstrated that broad temporal optical limiting can be accomplished with low limiting threshold by utilizing Fe_3O_4–Ag nanocomposites in solution. Due to the presence of Ag nanoparticles, nonlinear scattering gives rise to enhanced optical limiting responses to 532-nm nanosecond laser pulses, with a limiting threshold comparable to carbon nanotubes. As exposed to 780-nm femtosecond laser pulses, the largest value (approximately 10^{-44} cm^4s $photon^{-1}$ or 10^6 GM) for two-photon absorption cross-sections reported to date results in superior limiting responses with a limiting threshold as low as 0.04 J/cm^2 or 100 GW/cm^2. The limiting threshold can be further reduced by increasing Ag particle size through plasmon enhancement or taking advantage of self-defocusing. Taking into account the approximately 30 ps recovery time, Fe_3O_4–Ag nanocomposites are highly promising for optical limiting applications.

Although the foregoing invention has been described in some detail by way of illustration and example, and with regard to one or more embodiments, for the purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes, variations and modifications may be made thereto without departing from the spirit or scope of the invention as described in the appended claims.

I CLAIM:

1. A nanohybrid composite for use as an optical limiter, the composite comprising:

   - a first component selected for its giant two-photon absorption (TPA); and
   - a second component selected for its metallic properties to reinforce nonlinear scattering induced by nanosecond laser pulses and to greatly enhance TPA through its surface plasmon.