Rev. Adv. Mater. Sci. 40 (2015) 110-126

INVESTIGATION OF OPTICAL LIMITING IN NANOMETALS

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Received: April 19, 2014

Abstract. Fundamentals and Physical concepts of optical limiting (OL) phenomenon in nanometals have been reviewed in this manuscript.Two mechanisms of OL are based on nonlinear absorption and nonlinear refraction depends on the setup of the experiments. The effect of surface plasmon resonance (SPR) absorption of nanometals, as well as their size, shape, material, and concentration on their OL behavior are discussed in detail. Finally, OL phenomenon is investigated experimentally using gold and silver nanoparticles (NPs) suspensions in water, in low intensity regime. In addition, results based on the effects of laser intensity, aperture size, concentration, and size of Au and Ag NPs are presented.

1. INTRODUCTION TO OPTICAL LIMITING

1.1. Theory of optical limiting

As the names, an optical limiting is an effect to keep the power, irradiance, energy, or fluence transmitted by an optical system below the maximum value, regardless of the magnitude of the input. It must do this while maintaining high transmittance at low input powers. The most expanded applications of such an effect are the protection of sensitive optical sensors and components from laser damage. There are many other potential applications for such effects, including laser power regulation or stabilization, or restoration of signal levels in optical data transmission or logic systems, but this review will primarily concentrate on devices for sensor protection. In Passive systems [1], use a nonlinear optical material that functions as a combined sensor, processor, and a modulator. This offers the potential for high speed, simplicity, compactness, and low cost. The materials show the type of effects that produces optical limiting; but these effects prove not to be large enough.

Because of this, all prototypes demonstrated to date places the nonlinear optical component in or near a focal plane. In this focused geometry, material nonlinearities are barely large enough. Hence, research to date on OLhas focused on the search for new or modified materials with stronger nonlinearities, and on how to optimally use the best available nonlinear materials. Recently, nanometals are also one of the classes of the nonlinear materials these were shown significantly nonlinear effect.

An ideal optical limiter exhibits a linear transmission below the threshold, but above this limit, its output intensity is constant. The schema of an optical limiter and an optical switch are shown in Figs. 1a and 1b. Optical limiters have been utilized in a variety of circumstances where a decreasing transmission with increasing excitation is desirable [2]. While saturable absorbers had long been used for pulse compression, Q switching and mode locking, in 1984 Harter and Band demonstrated that an optical limiter consisting of a reverse saturable absorber [3]. Harter et al. have also shown that amplitude modulated pulses can be smoothed by an optical limiter, provided the duration of the amplitude

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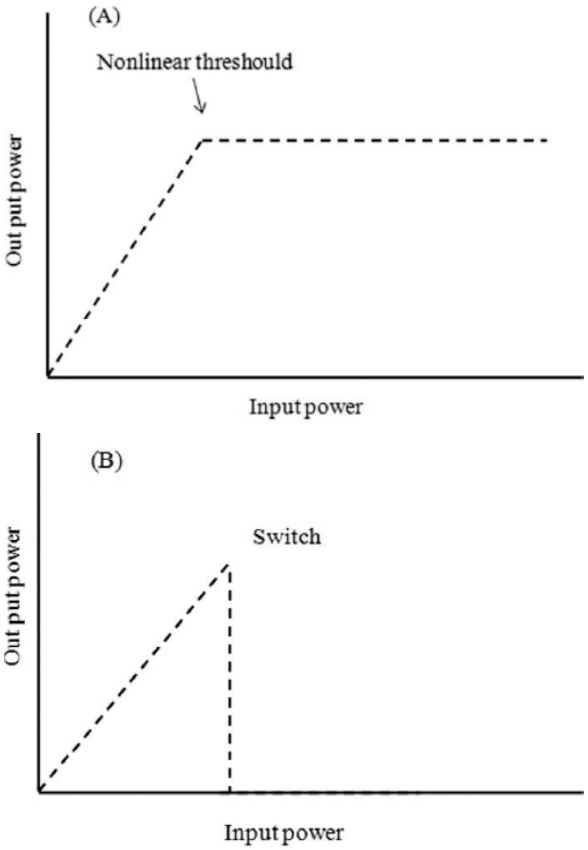

Fig. 1. (A) The optical response of an optical limiter to incident fluence (B) The optical response of an ideal optical switch to incident optical response of an optical switch, replotted from [2].

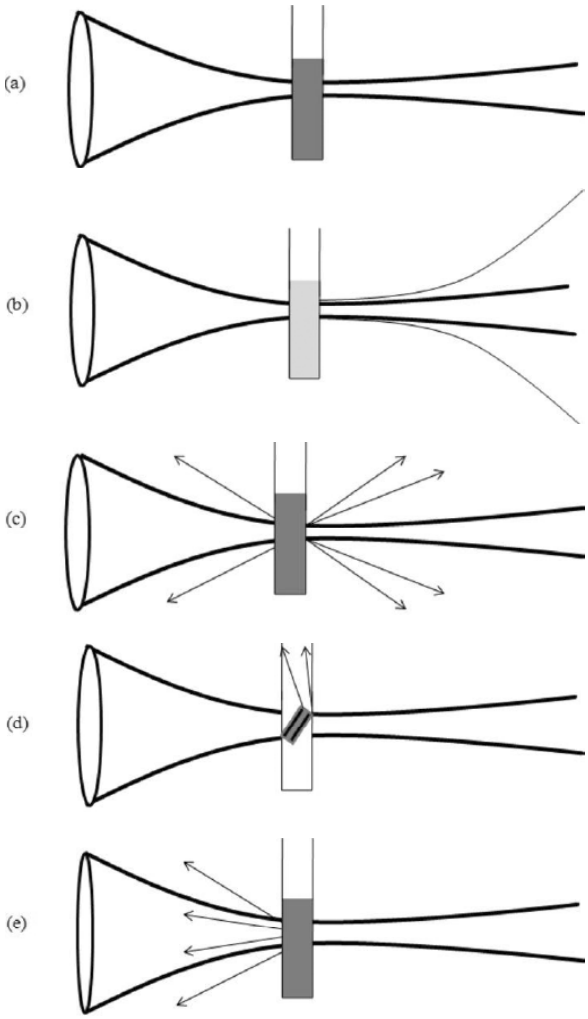

Fig. 2. Fundamental mechanisms for passive optical limiting: (a) nonlinear absorption; (b) nonlinear refraction; (c) nonlinear scattering; (d) photorefraction; (e) optically induced phase transitions, replotted from [1].

substructure is long compared to the activation time of the limiter [4]. In 1986, Band et al. demonstrated that an optical limiter could be combined with a saturable absorber for improved pulse compression [5].Yet another application of optical limiters has been proposed and demonstrated by Bialkowski [6].Several reviews of optical limiter materials have been published since 1989, including those by Wood et al. [7–9], Hermann and Staromlynski [10].

The variety of nonlinear optical phenomena can be used to construct an optical limiter. These include absorptive processes such as reverse saturable absorption, two-photon absorption, and free carrier absorption, nonlinear refractive processes such as self focusing, self defocusing, photorefraction, and optically induced scattering.

This paper includes three parts. Part one consists of introduction, OL applications, and its mechanisms. In addition, ideal and real OLs are compared. In the second part we have considered the physics of SPR effects on OL and the optical properties of nanomaterials are explained. In the third part, we have studied experimentally one of the OL mechanisms by low power laser and finally results are presented.

1.2. Mechanisms of OL

By introducing the passive optical limiting, we briefly describe the most common nonlinear mechanisms used. As presented in Fig. 2, these are (*a*) nonlinear absorption, (*b*) nonlinear refraction, (*c*) nonlinear scattering, (*d*) photorefraction, and (*e*) optically induced phase transitions. Here we concentrate on how each nonlinear optical property results in OL phenomena [1].

The OL effect of refraction nonlinear optical mechanisms, was induced the self focusing, self defocusing, scattering, refraction and aberration in nonlinear optical media. In this condition, the key

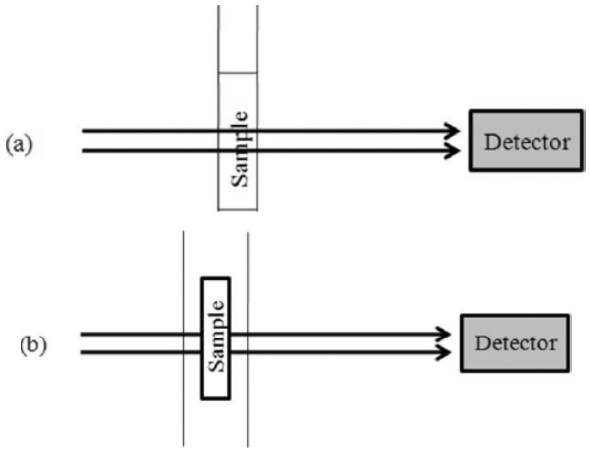

Fig. 3. Schematic of OL device based on nonlinear absorption and optical bistability, replotted from [11].

requirement is to place an aperture in front of a detector and the limiting of the detected laser beam is based on the fact, the spatial energy distribution of the transmitted laser beam has changed. When the input laser intensity increases, there will be more portions of the incident laser energy spreading as a result the portion passing through a small aperture will decrease accordingly. Consequently, all devices based on these mechanisms can be called the energy spreading type of optical limiters. In these cases, obviously, the observed OL behavior depends not only on the incident laser intensity and the nonlinear medium, but also on the pinhole size and the geometric configuration. For most of this type OL effect, the thermally induced refractive index change plays a major role.

Another type of mechanisms is the nonlinear absorption that can be employed for optical limiting. In this case, no aperture or pinhole is necessary, and the OLrelies on the fact that the transmissivty for some nonlinearly absorbing media decreases when the input laser intensity increases. There are two major nonlinear absorption mechanisms employed for OLthe one of is the reverse saturable absorption (RSA) and the other is the two-photon absorption (TPA). The based on these mechanisms can be called the energy absorbing type of the optical limiters. Using TPA as the OL mechanism exhibits the advantage of (i) negligible linear absorption loss for weak signal, (ii) extremely fast temporal response, and (iii) retaining high beam quality of the transmitted signal. For these reasons, TPA based devices are suitable not only for optical limiting, but also for other applicable purposes such as optical power stabilization, optical pulse reshaping, optical spatial field reshaping [11].

1.2.1. Nonlinear absorption in OL

For the device based on nonlinear absorption shown in Fig. 3, the observed OL behavior is essentially determined only by the nonlinear medium itself, provided that no aperture is placed and the sensitive area of the detector is considerable larger the laser beam size. In this case, the transmitted laser intensity I can be generally expressed as

$$I(z) = T(I_0).I_0, \quad (1)$$

where I_0 is the input intensity, $T(I_0)$ is the tranmissivity of the medium and it is a decreasing function of I_0. It is known that there are two major mechanisms that may lead to nonlinear absorption: one is the RSA, and the other is the TPA.

The RSA is a two-step and sequential one photon absorption process, as shown in Fig. 4a. In this case, a certain number of molecules are excited to an excited state 2. For a properly chosen medium, it is possible that the excited molecules will make a further transition from the excited state 2 to a higher excited state 3 via another N_2 in state 2 and the incident intensity I. On the other hand, N_2 is proportional to I and N_1,i.e.

$$N_2 \propto \sigma_{12} I N_1, \quad (2)$$

where σ_{12} is the cross section of the transition from the ground state 1 to the state 2. One can see from Eq. (2) that the following the increase I, the molecule number N_2 continuously grows and the se-

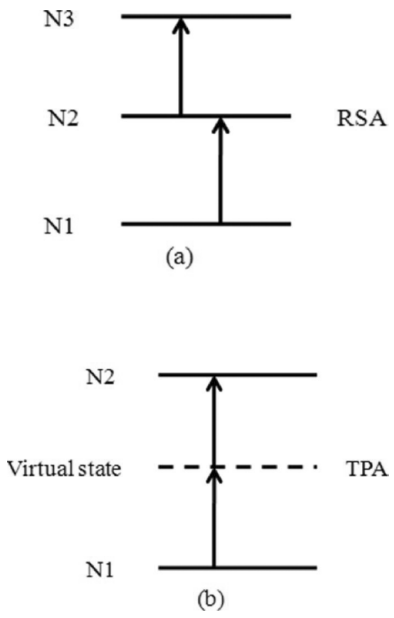

Fig. 4. Nonlinear absorption mechanism (a) reverse saturable absorption, (b) two photon absorption, replotted from [11].

quential one photon absorption due to the transition from state 2 to state 3 become more significant, provided that the cross section,

$$\frac{\mathrm{d}I(z)}{\mathrm{d}z} = -\sigma_{12}\left(N_1 - N_2\right)I_z - \sigma_{23}N_2 I(z). \tag{3}$$

In the simplest case, it can be assumed that $N_1 >> N_2$, $N_3 \approx 0$, where N_0 is the density of the absorbing molecules. Then according to Eq. (2), the above equation can be rewritten as

$$\frac{\mathrm{d}I(z)}{\mathrm{d}z} = -\sigma_{12}N_0 I(z) - b\sigma_{12}\sigma_{23}N_0 I^2(z) = -\alpha I(z) - \beta' I^2(z), \tag{4}$$

where β is a proportionally coefficient, and the linear absorption coefficient α_0 and nonlinear absorption coefficient b' are defined as

$$\alpha_0 = \sigma_{12}N_0, \tag{5}$$

$$\beta' = b\sigma_{12}\sigma_{23}N_0. \tag{6}$$

The solution of Eq. (4) is

$$I(z) = \frac{I_0 e^{-\alpha_0 z}}{1 + \left(1 - e^{-\alpha_0 z}\right)\dfrac{\beta'}{\alpha_0}I_0}. \tag{7}$$

If we assume that the linear absorption as small and $\exp(-\alpha_0 z) \approx 1 - \alpha_0 z$, Eq. (7) leads to

$$T(I_0) = \frac{I(z)}{I_0} = \frac{T_0}{1 + \beta' z I_0}. \tag{8}$$

Here, $T_0 = \exp(-\alpha_0 z)$ is the linear transmissivity of the sample medium for a weak input light signal, and $T(I_0)$ is the intensity dependent dynamic transmissivity of the same medium for a high intensity laser beam. From Eq. (8) we can see that the dynamic transmissivity decreases when the input intensity increases. This is the simplest quantitative description of RSA.

In the TPA process, the molecular transition from the ground state 1 to an excited state 2 is accomplished via an intermediate state that is represented by a virtual energy level, as shown in Fig. 4b. In this case, the laser intensity change due to both one photon and two-photon absorption can be expressed as Eq. (9),

$$\frac{\mathrm{d}I(z)}{\mathrm{d}z} = -\alpha_0 I(z) - \beta I^2(z), \tag{9}$$

where α_0 is the linear absorption coefficient of the medium at the incident laser wavelength, and β is the nonlinear absorption coefficient for the laser beam due to the TPA process. The further description of TPA behavior in OL performance will be presented later [11].

This equation is formally identical with Eq. (4), therefore we can immediately obtain the expression for dynamic transmissivity of the TPA medium

$$T(I_0) = \frac{I(z)}{I_0} = \frac{T_0}{1 + \beta z I_0}. \tag{10}$$

The free-carrier absorption is a phenomenon that is analogous to the excited state absorption in organic molecules. Indeed, it has similar qualitative characteristics to ESA. In semiconductor/band gap materials like photorefractive, the absorption of a photon with energy greater than the band gap will promote an electron to the conduction band. The excited electron will rapidly thermalize and relax to the bottom of the conduction band. From there it will recombine with an excited hole in the valence band after a characteristic recombination time. However, at sufficiently high intensities, while it is at the conduction band can absorb another photon. This process is called free carrier absorption. Once free carriers are generated in semiconductors, they may experience phonon-assisted absorption to higher lying (lower-lying) states in the conduction (valence) band. In the weak absorption regime, the attenuation can be described by

$$\frac{\partial I}{\partial Z} = -\alpha_0 I - \sigma_c N_c(I) I, \tag{11}$$

where $N_C(I)$ is the intensity dependent carrier density, and σ_c is the free carrier cross-section given by

$$\sigma_C = \frac{e^2}{\varepsilon_0 n_0 C m^* \omega^2 \tau}, \tag{12}$$

where m^* is the effective carrier mass, ω is the optical frequency and τ is the free-carrier decay time (mean collision time). The free-carrier density is governed by rate equation given by

$$\frac{\partial N_c}{\partial t} = \frac{\alpha_0 I}{\hbar\omega} - \frac{N_c}{\tau_c}, \tag{13}$$

where τ_c is the free-carrier relaxation time due to electron-hole recombination and carrier diffusion. In general, Eqs. (11) and (13) have to be solved numerically to determine the transmittance of the material. When the incident pulse is short compared

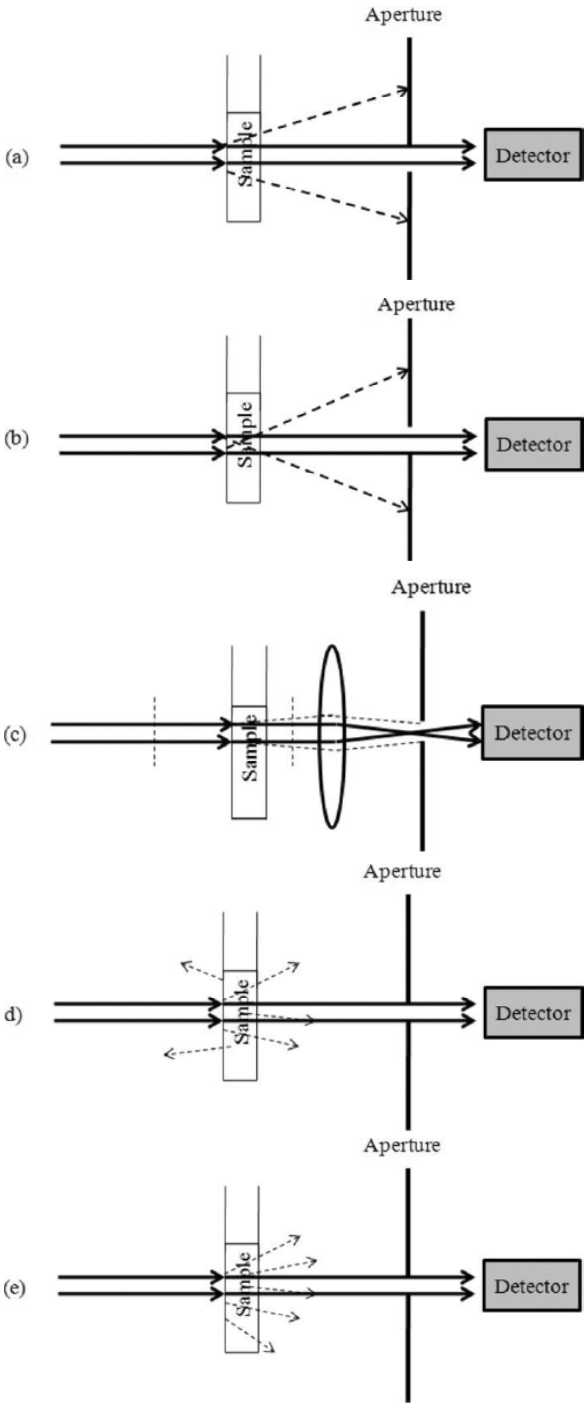

Fig. 5. Schematic illustrations of energy spreading type of OL, replotted from [11].

to the carrier relaxation time, second term in Eq. (13) can be neglected and Eqs. (11) and (13) can be integrated over time to obtain the flounce attenuation given by

$$\frac{\partial F}{\partial Z} = -\left(1 + \frac{F}{2F_s}\right)F, \tag{14}$$

where $F = h\omega/\sigma_c$, is the saturation flounce [12].

1.2.2. Nonlinear refraction in OL

Although there is a great variety of OL effect, most of them can be classified into two categories one is the energy spreading, and the other is the energy absorbing. Both types are the intensity dependent change in the beam structure and the spatial energy distribution of a laser beam passing through the nonlinear medium. At low intensity level, this change can be neglected and all laser beams can be detected through a properly placed aperture in front of a detector. Whereas at high intensity levels, this change becomes more severe and only a small portion of beam energy can pass through the aperture and be finally detected.In contrast, the principle of the second type of devices is the intensity dependent nonlinear absorption of laser energy in a nonlinear medium. In the laser case, the beam structure change is not essentially important and therefore; no aperture is needed.

The feature of the designs shown in Figs. 5a-5e is that the observed OL behavior for a given medium will strongly depend on the optical system configuration, as well as the size and position of the aperture [11].

From Kramers-Krönig relations, we know that all materials exhibiting nonlinear absorption must also exhibit nonlinear refraction. This can usually be expressed as

$$n_{eff} = n_0 + n_2 I + \sigma_r N_{ex}, \tag{15}$$

where n_2 describes instantaneous index changes proportional to incident irradiance and σ_r describes the change in the index due to population of excited states. Third-Order optical nonlinearities, n_2 is related to the TPA coefficient, β, by Kramers-Krönig relations. As a focused beam has a spatially varying irradiance, then the induced index change varies across the beam profile, causing the beam to be strongly distorted upon propagation. Near focus, the beam is usually brightest in the center, so for a negative index change (where the index decreases with increasing irradiance or fluence), the nonlinear material will behave like a lens with negative focal length, and the beam is defocused [1]. This process is referred to as *self defocusing*. If the sign of the index change is positive, *self-focusing* results [13]. An advantage of this method over nonlinear absorption devices is that there is no need to absorb large amounts of energy in the nonlinear material, which could cause thermal damage problems.

While we have concentrated the discussion in this section on nonlinear refraction associated with the electronic Kerr effect and, it should be noted

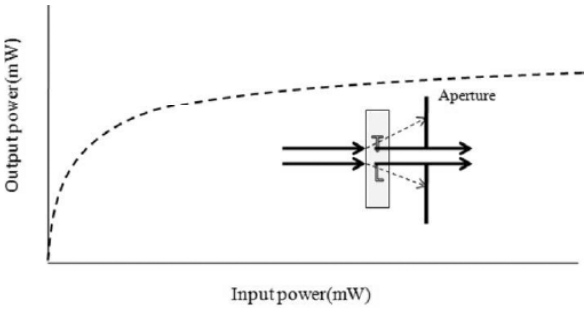

Fig. 6. Power though the aperture as a function of the input power of 488 nm Ar laser. The thermal lens formed in the 1 cm long nitrobenzene liquid cell, replotted from [11].

that many other processes, such as molecular reorientation, absorption saturation, and optically induced heating, can also lead to refractive nonlinearities that can be used for OL [2].

1.2.2.1. Opto thermal effect based optical limiting

It is clear that all OL devices of energy spearing type are essentially based on the laser induced refractive index change. In this situation, partial energy of the laser beam is transferred to the medium, becomes thermal energy, and finally causes the local temperature increase. For example optical set up and the detected power as a function of input power is shown in Fig. 6. It was noted that the change of power through the aperture was only 3% of the total input power change at high input levels.

The major contributions to the observed OL behavior are summarized as follows:

a) In any transparent, there always exist small amount of impurities, which give rise to a nonzero residual linear absorption. If the incident light is an intense CW laser beam or pulsed laser beam with high flounce, the small residual linear absorption might be strong enough to create a remarkable thermally induced refractive index change.

b) If the medium is a resonant and linearly absorbing material, the thermally induced refractive index change can be readily significant even for low flounce laser beam.

c) If the medium is a nonlinearly absorbing material, and an aperture, the contribution of the thermal effect may be more responsible for the observed OL behavior [11].

In solids, temperature dependence of the absorption edge can lead to thermally induced index changes. These usually result in an increase in index with temperature. In liquids, the index change results from the change in density upon heating lead to laser absorption. Therefore, the index decreases with temperature, giving a self-defocusing effect [1].

1.2.3. Comparison ideal optical limiter and realistic optical limiter

The ideal optical limiter is illustrated in Fig. 7a. For some materials, e.g., two-photon absorbers, this transmittance may be near 100%, and the input–output curve would have a slope of 45°. On the other hand, RSA materials require a certain amount of linear absorption, and thus the input–output slope in the linear regime <45°. At some critical intensity or threshold in an ideal limiter, the transmittance changes abruptly and exhibits an inverse intensity or fluent dependence.

In a real material, illustrated in Fig. 7b, this transition is not so abrupt. The definition of threshold is not precise. In addition, in a real material, the output is not always clamped at a constant value, but the input–output slope is decreased as shown in Fig. 7b.Thus, if the input–output slope is nonzero, at some input above threshold the device will fail to provide protection. In some cases, the material itself may be damaged if its damage threshold is below this point, or the intensity/fluence dependent transmittance may approach a constant asymptote so that the input–output slope again increases [12]. In summary, we have attempted present state of OLprimarily for eye and sensor protection. Further

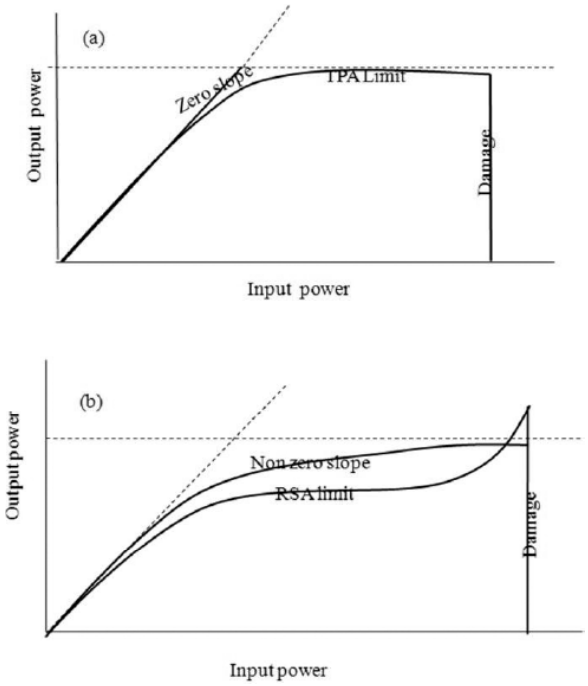

Fig. 7. Input–output characteristics of an optical limiter.(a) Ideal optical limiter and (b) realistic optical limiter, replotted from [12].

material research is clearly required to enable expanded sensor protection as well as new applications for these devices.

2. PHYSICAL CONCEPT OF SPR

SPR is important optical property of metallic nanostructures. This effect arises of a collective oscillation of conduction electrons excited by the electromagnetic field of light [14-16]. In the case of metallic NPs, the electron oscillations induce an electric field around the size of NP that can be much larger than the wavelength incident light. The optical properties of NPs are modified by the appearance of SPs that its behavior is completely different from the bulk metal one. The SPs effect open the possibility to amplify, concentrate, and manipulate light at the nanoscale, overcoming the diffraction limit of traditional optics and increasing resolution and sensitivity of optical probes [17].However, SPs are the finite size can be used in a wide range of fields, including energy [18-20], environment protection [21-23], biomedical [24-27], and information technology [28] applications.

The ultimate goal will be the determination of the frequency of the absorption maximum (denoted ω_M, the frequency of the Mie resonance), the height of this maximum and the width of the peak. This electronic motion is specific of NPs due to geometrical confinement effects of the free electrons. Indeed a nanometal can be seen as an immobile and periodical cationic network in which a cloud of conducting electron moves. The latter is usually considered as free electrons [29].

2.1. Investigation of the SPR effect induced by OL in nanometals

Whatever the nonlinear process involved, the nanometals have been inquiring for their OL properties, owing to the important stake that such functionality represents for civil and military applications in human eye or detector protection.Indeed, as for telecom applications, metal NPs present the advantages of both intense and fast nonlinear responses.

Fig. 8 shows selected results from OL properties of materials containing gold or silver NPs. All kinds of materials roughly present the same OL efficiency, with varying thresholds, apart from C_{60} type Au in chloroform (sample *i*) which appears better than C_{60} in toluene, a compound which is yet itself known for its high OL ability. A similar result was established by the fullerene-silver nanocomposites

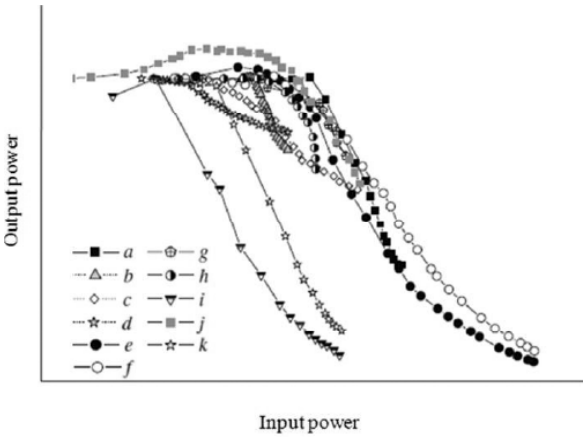

Fig. 8. Normalized transmission as a function of laser fluence for material containing gold and silver NPs, replotted from [30].

(DTC_{60}-Ag) in hexane. The strong OL is expected by the authors to originate from the excited state interaction between the fullerene and metal NPs. Also notice the special case of material *j* (Au NPs in glass excited at the SPR by 8 ns pulses): Transmission begins to increase (SA phenomenon) and then decreases as the input fluence rises. François et al. studied the influence of particle size on the OL performances of gold colloidal solutions excited by nanosecond pulses at the SPR, in the range are R = 2.5–15 nm. They found that, as R increases, both the OL threshold and amplitude increase. Moreover, they reported later the influence of wavelength on the OL efficiency, and established that the latter is as high as λ is close to λ_{SPR} [30]. In addition Gao et. al show the optical properties of nanoscale metal domains are strongly influenced by the SPR absorption. This is relevant for the case of OL where the material's absorption is dependent on the intensity of input laser. It has also been found that a laser pulse can cause an interband or intraband electron transition in the nanometal system depending on the excitation wavelength and intensity. The electrons thus excited are free carriers that can lead to transient absorption. Therefore, besides strong excited-state absorption, SPR absorption and free carrier absorption can occur and contribute to the OL in C60tpy-Ag NPs. On the other hand, nonlinear scattering of nanometal plays more important role in OL [31].

In summary, two mechanisms may be considerable for OL of metallic NPs [32-33]. One is attributed to the SPR induced by the photoexcitation and oscillations of the free electrons in the conduction band that occupy energy states near the Fermi level [34,35]. In general, the SPR of metallic NPs, de-

pending on the metal species, their shape, and surrounding medium [36]. Another mechanism is attributed to interband or intraband electron transition caused by laser pulses, depending on the metal species, the excitation wavelength, and intensity [34]. The contributions of the interband transition to optical nonlinearities come from the photoexcitation of electrons out of the d band near the X point of the Brillouin zone to the s–p-conduction- band states near the Fermi energy [37]. These mechanisms physically are under the influence of size, concentration, shape and morphology of metallic nanoparticles in suspensions, which are going to be reviewed in detail.

Y. Gao et al. have study the OL performance in gold NPs with different size at 532 nm for 8 ns laser pulses. This investigation may be helpful for the synthesis of metal NPs for optical limiting [38].R. B. Martin et al. report a systematic OL investigation of the silver and silver sulfide NPs with different average particle sizes and size distributions [39].Taking advantage of the strong wavelength dependence of the optical spectrum of metal clusters, L. François et al. performed experiments at various laser excitation wavelengths. The results obtained at various wavelengths for different particle sizes and at different timescales allow them to propose a mechanism to explain the nature of the light scattering centers, which are responsible for the optical limitation [40]. P. Zhang et al. reported that a C_{60} mono-derivative (DTMF) with a hydrophobic–hydrophilic–hydrophobic structure could self-assemble into nanospheres in water. Indeed, gold NPs can be in situ assembled onto the surface of DTMF spheres, resulting in gold nanoparticle-modified DTMF nanospheres [41]. R.A. Ganeev et al. presented the investigations of nonlinear optical parameters of colloidal metal solutions (Ag, Pt, Au, Cu) [42]. Such media are of great interest due to their possible applications in optical modulation and the OL of laser radiation. S. Mohapatra et al. reported the synthesis of Cu–silica nanocomposite thin films. The effects of metal fraction on the SPR absorption and the nonlinear optical properties of nanocomposites are investigated in this report. In addition, size-dependent, low frequency, in Cu NPs has been investigated and optical-limiting response is reported [43]. R. Sreeja et al. presented the gold NPs showing better nonlinearity are embedded in a stable polymer matrix so as to yield ease of flexibility as well as long-term stability in a device point of view as compared to the metal nanocolloids. They show UV/visible absorption spectra arises of SPR bands are red shifted in wavelength when increases particle size. Then optical absorptive nonlinearity of the nanoclusters shows an optical-limiting-type nonlinearity, that the efficiency of limiting decreases with an increase in particle size [44]. Q. Yang et al. investigated the optical properties of Au NPs with PVP surfactant in water. It was found that Mie scattering theory could be used to describe the linear optical properties of these samples very well. The absorption peaks and FWHM of the SPR may be used estimate the size of the gold NPs with good accuracy. This provides a convenient, easy to handle way to size the gold NPs [45]. S. Qu et al. obtained the Au NPs contained glasses by a femtosecond laser. Inside these glasses, the sizes and space distribution of the Au NPs were induced by controlling the irradiation conditions of the femtosecond pulses. The difference in the OL capability at 532 nm for these samples arises mainly from the different plasmon absorption strengths changed by their dissimilar particle sizes [46].

S. L. Smitha et al. reported the synthesis of Au nanorodes of different aspect ratios by a seed mediated technique. They are discussing the influence of various parameters like the silver ion concentration ascorbic concentration and PH of the growth solution on the aspect ratio of the Au nanorods [47]. In addition, H. Nadjari et al. produced silver and gold nanocolloid with ablation of their metal foil in pure water. These samples have nearly the same concentration and spherical shape [48]. H. Aleali et al. reported on the experimental investigation of OL of gold NPs dispersed in the castor oil. The threshold-tunable optical limiters in the AuNPs colloids are demonstrated experimentally due to the parameters of the set-up and concentration of gold NPs [49]. J. Z. Anvari et al. reported on the designing low threshold optical limiters of copper NPs dispersed in polysiloxane oil. The limiting threshold can be improved by making an appropriate choice of design geometry of the configuration [50]. R. Karimzadeh et al. reported on measurements of the effective thermal nonlinear refractive index of the silver sulfide NPs (Ag_2S NPs) dispersed in the dimethyl sulfoxide (DMSO).The limiting threshold as a function of concentration of the Ag_2S nanocrystals is reported [51].The well-dispersed silver colloidal solutions have been prepared through in situ synthesis technology in the presence of PMMA by Y. Deng et al. and their nonlinear optical properties were studied for different silver concentration. These solutions have been observed to have the same average particle size, thus giving a wide variety in the particle density by changing the amount of $AgNO_3$. The optical nonlinearity was enhanced with the increase of sil-

ver NPs concentration, which was ascribed to the SPR enhancement mechanism [52]. Y. Gao et al. investigated OL properties of the nanomaterial.The optical properties of nanoscale metal domains are strongly influenced by the SPR absorption. This is relevant for the case of OL where the materials absorption is dependent on the intensity of input laser. It is clear that the OL threshold and clamped level decrease with the increase of the concentration [31]. M. Eslamifar et al. experimentally investigated the linear absorption measurement using a low power laser [53,54] in order to understand and to model the processes leading OL action.

S. Qu et al. investigated the nonlinear absorption and OL properties of two gold nanorods. The experimental results obtained significantly depend on the sizes of two nanorods. As is analyzed above, the two gold nanorods when excited at 532 nm can result in the strong transverse plasmon absorption followed by the excited-state absorption, which induces the transmittance to decrease with increasing intensity of the laser [55]. V. Liberman et al. designed and characterized experimentally as well as computationally nanostructures that are optimized for nonlinear electric near-field enhancement. By analyzing nanostructures with various degrees of enhancement over a broad wavelength range, they show that the observed OL effect scales with the plasmonic enhancement of the nanomaterial. They furthermore suggest that proper optimization of SPR should lead to a rational design of nanostructures optimized for optical limiting. The NPs of Ag and Au have been shown to exhibit OL behavior, which can be described phenomenologically as the result of nonlinear processes. Nanourchins prepared of Au has a nonlinear cross section that is at least 100× higher than that of the corresponding nanospheres. While nanourchins do possess a complex geometry, they offer flexibility in manipulating the position and the strength of plasmonic resonances via spine length manipulation. Furthermore, because of the multiplicity of the spines, urchins have an increased probability of favorable alignment with the incident electric fields, as compared to simpler shapes such as nanorods [56].In the paper was received by R. Sathyavathi et al. reported, biosynthesis of the Ag NPs using Coriandrum Sativum Leaf extract as a reducing agent and demonstrate that this method yields faster and stable silver NPs compared to other methods. The SPR effect, which plays an important role in enhancing the optical nonlinearities, can be altered by changing the size, shape, and volume of the particle [57]. S. Qu et al. presented the nonlinear refraction and OL effect of gold nanorods. Since 532-nm irradiated gold nanorods should result in strong transverse plasmon absorption followed by the excited-state absorption, the transmittance of the sample would decrease with increasing laser intensity. Therefore, they can infer the strength of plasmon absorption of gold nanorods from the OL effect [58]. H. I. Elim et al. reported their investigations of resonant, SA, and RSA of longitudinal surface plasmons in gold nanorods (Au NRs). These interactions induce the further excitation of the hot electrons around the SPR peak [59].

P. Sudheesh et al. attributes the optical power limiting of the composite films [60]. R. A. Ganeev et al. present results of investigation of the OL in fullerene solutions, colloidal metals, and semiconductor structures irradiated by the fundamental and second harmonics of pico- and nanosecond pulsed radiation of a Nd:YAG laser [61]. S. Porel et al. reported the OL capability of Au-PVA film. The convenient formation of metal nanoparticle polymer composited with control of the nanostructure and appreciable nonlinear optical response of the thin film material are significant from the perspective of device applications [62]. In this paper the preparation of silver NPs in a mixed solution $AgNO_3$ and TiO_2 was reported by H. Zeng et al. Indeed, the TiO_2 sol played the key role of promoting the formation of silver NPs [63]. X. Zhang presented their studies of nonlinear optical properties of silver colloids [64]. Metal nanowires have been grown by H. Pan et al., they have presented that the OL properties of Pt, Ni, Pd, and Ag nanowires are better than those of Cu and Co nanowires [65]. A.I Ryasnyanskii et al. note that the optical limitation in metal hydrosols scarcely studied.This process is mainly caused by the two-photon light absorption due to the SPR of gold hydrosol in the region of 565 nm; such absorption corresponds to the two-photon transition at the wavelength of 1064 nm [66]. In addition, K. M. Rahulan et al. presented nonlinear optical studies on the PVP stabilized Ag nanocolloids. The results obtained in the present experiment render practical applicability to the nanocolloids as optical limiters, which will be explained, taking into account the SPR band bleach and absorption. Moreover, size of metal NPs, the nature of the host matrix, metal concentration, and optical intensity influences the optical non-linearity of NPs [67]. L. Irimpan et al. reported the wavelength dependence of nonlinear absorption of ZnO-Cu nanocomposites with varying Cu content under nanosecond excitation. It is also known that doping significantly improves the limiting performance of ZnO. The nonlinear optical response is

studied, which includes the SPA band. Such a change over in the sign of the nonlinearity of ZnO-Cu nanocomposites, with respect to Cu nanocolloidsis related to the interplay of Plasmon band bleach and OL mechanisms [68]. S. Qu et al. principally investigate the OL performance of microstructures containing Au particles in silicate glasses obtained. Since the plasmon and free carrier, are broadband in nature with the primary absorption [69]. S. Qu et al. have also observed strong OL behaviors in nanocomposites. They investigated the optical nonlinearities of three nanocomposites with noble metal gold naonoparticles by OL experiments, while the SPR could mainly be responsible for the stronger self-focusing effects. Optical nonlinearities in these nanocomposites can be attributed to the strong excited state absorptions of the ligands and the SPR of gold NPs [70]. H.Fang et al. reported that two novel [60] fullerene derivatives containing the Olig Opyridyl group have been synthesized and self-assembled on the surface of gold NPs to investigate the nonlinear optical responses. They suppose that it results from the SPRof the gold NPs caused by light excitation [71]. P. P. Kiran et al. reported the NLO properties and the role of the SPRtoward the OL properties of Ag-Cu nanocluster co-doped in SiO_2 matrix. The OL properties of these nanoclusters were investigated at three different wavelengths to understand the contribution of SPR toward it [72]. S. Qu et al. investigated the OL property of PVP stabilized platinum nanoparticles and propose a model OL based on Mie excitation theory [73]. R. Philip et al. showed that at moderate pump intensities samples exhibit a saturable absorber behavior, whereas all samples show strong OLat still higher intensities.Therefore, since the bleach recovery of the ground-state plasmon band is generally in the order of picoseconds, they can also be used as fast optical switches [74]. M. Anija et al. discuss the features of nonlinear optical transmission observed in the clusters $Ag@ZrO_2$, $Au@SiO_2$, $Au@ZrO_2$, and $Au@TiO_2$ suspended in 2-propanol, when excited.Results show that the samples have a high laser damage threshold and can be used as optical limiters in the appropriate laser fluence regimes. Resonant excitation with nanosecond and longer pulses can result in thermally induced transient refractive index changes [75]. In this work, E. Messina et al. report a systematic study of the effect of the ablation parameters and reirradiation treatment on PLA Ag/Au colloids optical properties using different spectroscopic techniques.They were able to synthesize contaminant free Ag-Au composite nanostructure with tunable plasmon resonance. In particular, a reduction of the limiting threshold was observed by increasing the gold content [76]. In the paper of S. Nair et al. a single step synthesis and characterization of $Au_xAg_y@ZrO_2$ core–shell alloy NPs of varying composition is reported. A reduction in transmission can occur due to a number of phenomena, and the prominence of each will depend on the sample, excitation wavelength and laser pulse width [77]. In addition A. Lin et al. report on the OL behaviors of Au NPs incorporated in germanosilicate glass fibers having SPR absorption band positions in the visible wavelength region. The results demonstrated that the effective nonlinear absorption coefficient around the SPR absorption peak of the gold-NP incorporated fiber was almost ten times that of a reference fiber without any dopant and that at the same time, and the OL threshold remarkably decreased [78]. C. Zhan et al. reported the near-IR picoseconds optical nonlinearity from 1-dodecanethiol stabilized gold NPs (Nano-1). Colloid silver NPs exhibit a strong and broad transient absorption in the visible and near- IR wavelength region when subjected to laser pulse excitation [79]. M.R.V. Sahyun et al. studied similar photo induced redox process was proposed to be responsible for the optical limiting characteristics of silver bromide nanosols comprising nanoparticles of silver bromide [80]. S. Qu et al. report experimental results of nonlinear optical responses in two novel gold NPs reported by ligand.The differences in OL effects for the nanocomposites are mainly due to the different number densities of gold NPs. Then can be attributed to relatively strong nonlinear refraction, nonlinear absorption and nonlinear scattering induced by the surface plasma resonance of gold NPs and the excited-state nonlinearities of ligand C_{60}tpy [81].

After the detailed discussion of OL, we investigated a case of the state mentioned. Therefore, we report on the experimental investigation of OL properties and the thermo-optical nonlinear response of gold and silver NPs dispersed using CW laser irradiation at 532 nm. The threshold-tunable optical limiters based on thermal nonlinear refraction in the Au NPs and Ag NPs colloids (laser ablation technique) are demonstrated experimentally due to the parameters of the set-up (aperture diameters, distance from the focal point), size, and concentration of noble metal NPs.

3. EXPERIMENTAL TECHNIQUE OF OL

Metal NPs were prepared by nanosecond pulsed laser ablation and optical properties of the

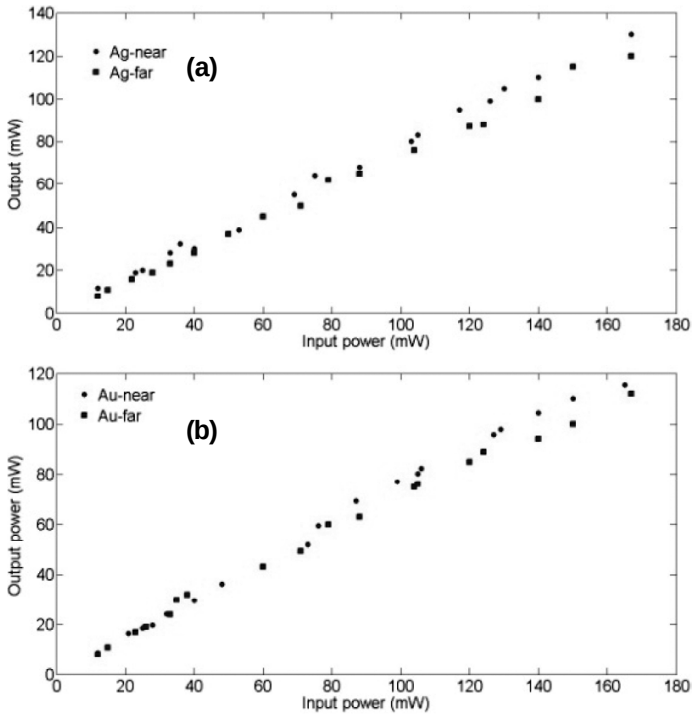

Fig. 9.Transmission of sample (2) at focus without aperture measurement in near and far from the focal point in (a) Ag, (b) Au.

nanoparticles reported in elsewhere [82,83]. In the first step at the absorption OL set up, sample 2 was placed at the focal point, where OL measurement was performed at near and far from this point. In a second step, the samples were placed at the three positions: the valley, peak and focal point of normalized transmissions for the refractive OL measurements.However, the radius of the aperture is 0.25 mm, 0.4 mm, 1.5 mm, 2 mm that placed before detector in order to monitor the transmitted energies. In the open OLmeasurement, do not need aperture, however head of power meter transition of the laser beam. The samples were placed at the focus point of the lens with the same former focal length.

3.1. Result and discussion

The linear extinction spectra of the nanospheres in the spectral range from 200 to 1100 nm were measured. The extinction spectra of NPs for sizes below 100 nm are dominated by dipolar absorptive Mie resonances, whereas for larger sizes, higher-order excitations and scattering losses begin to contribute [84].

In the absorption OL experiment low power Nd:YAG laser was used for the 532 nm wavelength region; the samples were placed at the focal point of the lens. Therefore, the low power laser beams cannot cause electron excitation, hence observe the nonlinear absorption effect cannot be observed. Fig. 9 demonstrates that the increase in the input intensity leads to linear increase in output intensity, this is the absolute effect of linear absorption. The width broadened laser beam (lead to scattering) is smaller than the head of power meter. The OL of each metal for near and far field zone are presented in this figure. The diffraction increases with the increase in the distance between the detector and focal point; this arises from the beam broadening and from the decrease in the detected power of the beam. With increasing the input power, the output power is increased linearly. In other words, the input power is not enough for absorption OL to be appeared.

In addition, we considered the OL experimental results of the colloids for different aperture sizes.It is clear here that the transmitted energy decreases with decreasing diaphragm size. This aperture dependence indicates that the nonlinear scattering may also play important role in the observed OL performance of the metal NPs. Effects of aperture on the OL of Ag NPs and Au NPs are shown in Fig. 10. For the 0.25, 0.4, 1.5, and 2 mm apertures, the OL power of Au NPs are 1.1 mW, 1.5 mW, 4 mW, 11 mW, and 13 mW respectively. These magnitudes are larger for Ag NPs which are 1.5 mW, 4 mW, 11 mW, and 13 mW due to the closer Au SPR wavelength to laser wavelength.

Moreover, the value of the limiting threshold of the colloids can also be tuned by changing the metal

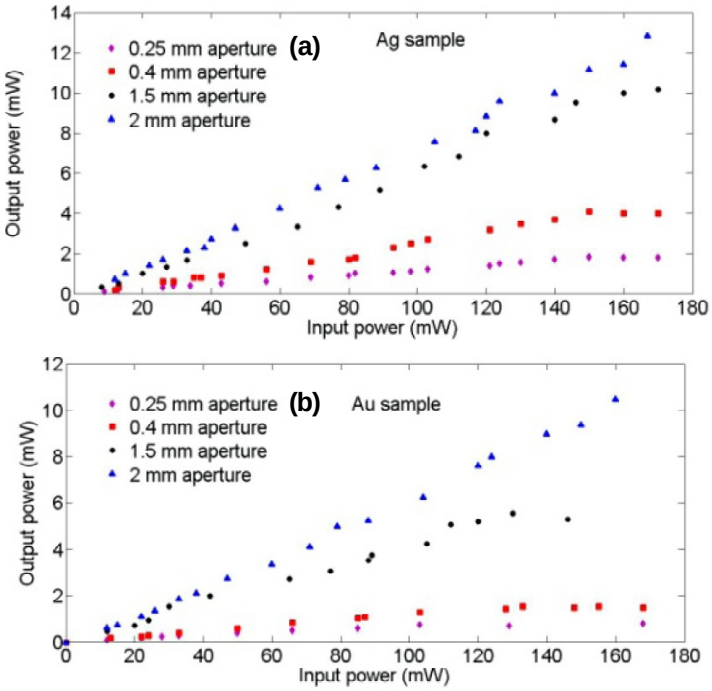

Fig. 10. Transmission of sample (2) at focus with aperture at 0.25, 0.4, 1.5, 2 mm in (a) Ag, (b) Au.

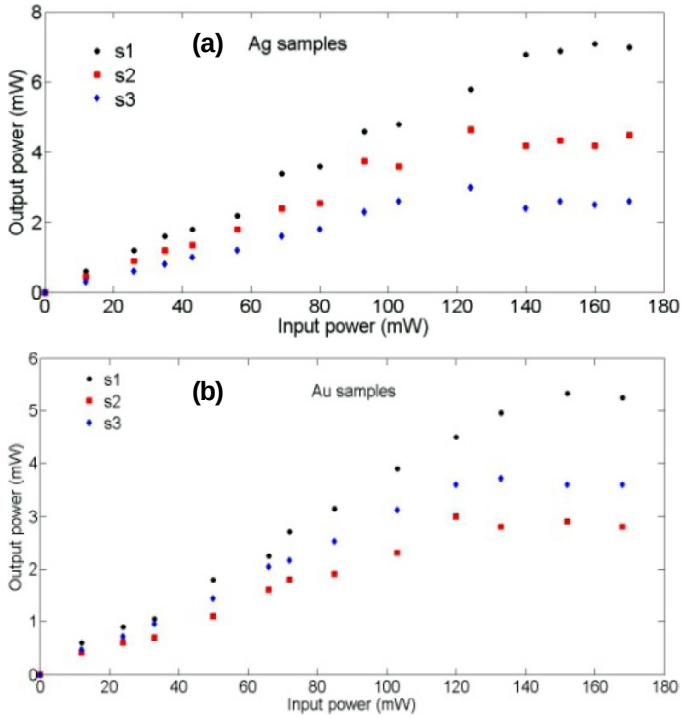

Fig. 11. Transmission of samples at focus with aperture at 0.4 mm in (a) Ag,(b) Au.

nanoparticle concentrations as shown in Fig.11. With increasing concentration of Ag NPs, Au NPs the limiting threshold is decreased. Our results indicate that the OL threshold value can be tuned by modifying the parameters of the set-up and the concentration of the metal NPs.It is plausible to understand the enhancement of the limiting response at high concentration as an increase in nonlinear scattering sites. At higher nanoparticle concentrations, metal NPs provide denser initial sites for the formation of bubbles. Thus, more bubbles in the focal volume are to be expected during laser irradiation of high concentration colloids, and this will promote a quicker increase in nonlinear scattering [85]. In samples 1 and 2 of gold nanoparticles with increasing the concentration of nanoparticles in suspensions, the threshold point of OL decreases, but in the case of sample 3 it didn't occur. In the case of

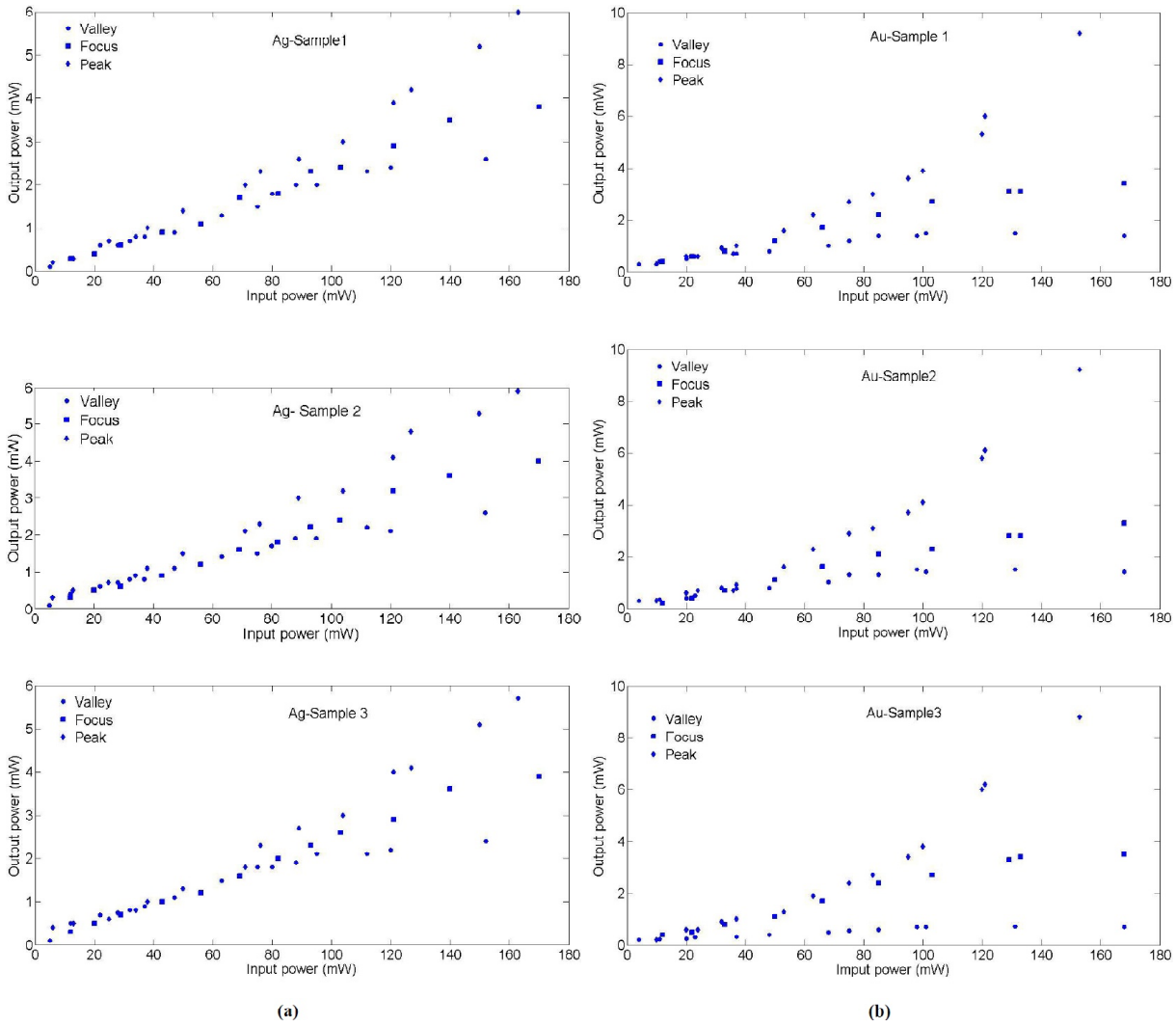

Fig. 12. Transmission of samples with aperture at 0.4 mm in (a) Ag, (b) Au.

sample 3, the concentration and size of NPs in the suspension is larger than for other samples. As was predicted, the size of nanoparticles is increased due to the presence of bubbles, this leads to the absorption decrease due to SPR effect and the increase in the threshold power of OL. Actually, the increase in the particle size will increase the SPR effect.

However, in the case of Ag samples this process can not be observed, because thermal effect in these samples is small. At this point, one need to consider the contribution of the nonlinear scattering, which may play important role in the observed nonlinearity of the NPs suspension.

In Figs. 12 and 13, we can see that the OL results are different for various positions of the samples. When the sample is placed at the peak, the optical limiter cannot work until the input power exceeds the threshold value of thermal self-diffraction. When the sample is placed at the focal point and valley, the OL effect occurs in the low power that is due to self-defocusing phenomena. Fig. 12 shows the result of OL experiments obtained by using 0.4 mm aperture. The threshold power of OL at valley is the smallest one in comparison with this magnitude at focus and peak points. In the case of 1.5 mm aperture, the similar phenomenon was also observed, it is shown in Fig. 13. Having OL with minimum threshold energy in the valley is a feature of nonlinear optical behavior of metallic NPs such as Ag and Au.

Both self-defocusing (scattering) and self-focusing effects can be used for optical limiters. The rays will deflect from the detector because of nonlinear refraction. The optimum position of the sample when it is used as the optical limiter based on self-defocusing effect is valley point. Therefore, when the nonlinear scattering was the dominating mechanism, the variation associated with the NPs (scattering centers) parameters would change the OL responses significantly [39]. Indeed, the optical lim-

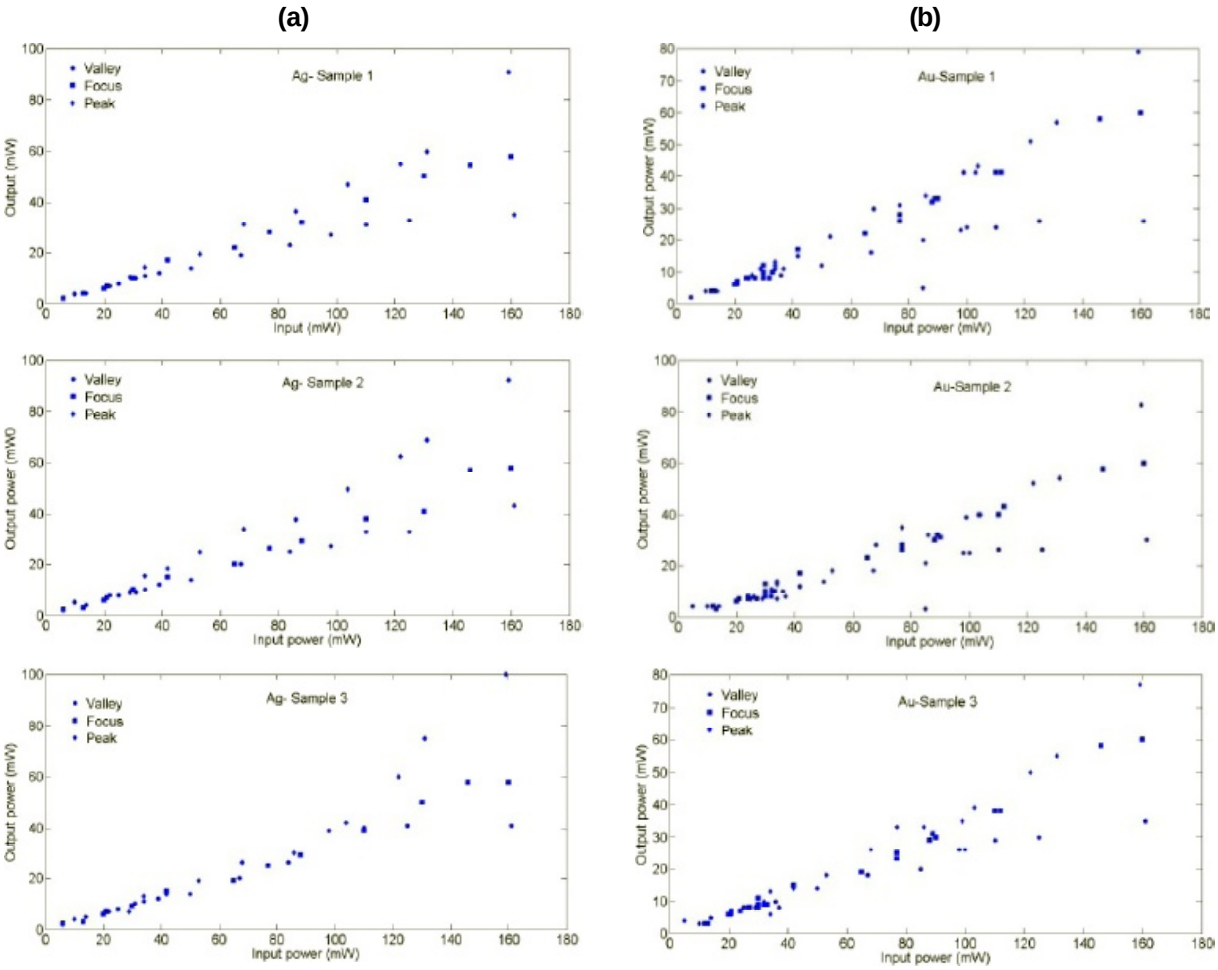

Fig.13. Transmission of samples with aperture at 1.5 mm in (a) Ag, (b) Au.

iting behavior in this experimental condition is due to scattering phenomena because of thermal effects caused by SPR.

3.2. Conclusions

In the considered experiments, the OL response was dominated by the nonlinear refraction mechanism. The ability and threshold value of the optical limiters can be optimized with changes in the experimental set-up and the metal NPs concentration of the colloids. We investigated the optical nonlinearities of three samples of gold and silver nanoparticles by OL experiments. The nonlinear optical response of thermo optic origin exhibited by NPs at low CW laser powers was studied [86]. The efficiency of limiting increased with a decrease in the particle size [87]. On the other hand, the OL threshold level decreases with increasing the nanoparticle concentration. The scattering effect observed in these samples under CW illumination was utilized to demonstrate their OL limitation [88]. In addition, the variation in the output intensity was studied as a function of input intensity for four different aperture sizes and the influence of the aperture size on the threshold limit and output-clamping power was analyzed. In the case of using aperture, there are three positions: valley, focus, and peak. At valley, the threshold of OL decreases. Because of diffraction, the input power decreases noticeably with the increase in the distance of the detector from focal point. However, our results show that without aperture, the power of CW laser is not enough for nonlinearity of Au and Ag NPs to be observed.

The OL threshold obtained is at mW, so it is a low power OL [89]. The limiter threshold can be improved by a proper choice of design parameters such as the geometry of the configuration and the concentration of the solution, based on the actual requirements of the sensor. This material is expected to be a suitable candidate for sensor protection in the CW low power regime, particularly where the response time is not of much significance [90].

When the laser power increases to a certain value, the self-defocusing is dominated by the thermal effect, which is closely related to the absorp-

tive (SPR) properties of the medium. The thermal self-diffraction can be observed if the sample is placed just behind the focal point. The self-defocusing induced by thermal effect can be utilized for constructing OL [91].

4. SUMMARY

In this work, we have attempted to provide a broad overview of the present state of OL primarily for eye and sensor protection. We have discussed a variety of nonlinear mechanisms, including reverse saturable absorption, two-photon absorption, free-carrier absorption, nonlinear refraction, and optically induced scattering, which have been applied to OL devices. We concluded that the presence of the SPR in metallic nanoparticles is the main responsible for their OL behavior. Finally, we presented the results of our experiments on the optical behavior of Ag and Au nanoparticle using low power CW laser.

If the nonlinear scattering was the dominated mechanism in optical limiting, the variation in the NPs parameters would change the OL responses. We showed that the optical limiting behavior in this experimental condition is due to scattering phenomena because of thermal effects caused by SPR.

The variety of nonlinearities and material configurations that have been used to implement passive optical limiters, no single device or combination of devices has yet been identified that will protect any given sensor. In this case metalic NPs and nanocomposites will be the base if the new generation of optical sensors. The advantages of new generation sensors are their dynamic range over which protection can be afforded, the field of view of the sensor, the physical dimensions of the limiter, threshold energy for activation, wavelength and pulse regimes for protection [2].

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