Noble metal nanoparticles and composites for nonlinear optics and its applications - A technical analysis and short review

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Abstract

Designing of the experiments and devices based on the nonlinear optics is a new and emerging field, which is finding newer applications. Technical analysis of the phenomenon associated with the nonlinear optics (NLO), like, for exmple: Second harmonic generation, Sum frequency generation, difference frequency generation, optical parameter amplification, 'N' wave mixing, and nonlinear polarization, has been presented in this paper The important materials studied and used for this fascinating field, the experimental results available in the literature and the related applications have also been reviewed. Optical nonlinear properties of noble metal nanoparticles and composites, and their applications for ultra-fast active plasmonics, and medical therapy have been discussed. The paper should be of great use for the new researchers entering this field, and also for the experts engaged in designing of the NLO based devices.

Keywords: Nonlinear optics (NLO), optical nonlinear properties of Noble Metal nanoparticles and composites, ultra-fast active plasmonics.

Resumen

El diseño de los experimentos y los dispositivos basados en la óptica no lineal es uncampo científico nuevo y emergente, que está encontrando nuevas aplicaciones. El análisis técnico del fenómeno asociado a la óptica no lineal (ONL), como, por ejemplo:La segunda generación de armónicos, la generación de la suma de frecuencias, la generación de diferencias de frecuencias, la amplificación del parámetro óptico,la ola de mezcla tipo 'N', y la polarización no lineal, se han presentado en este artículo Los importantes materiales estudiados y utilizados en este fascinante campo de estudio, los resultados experimentales disponibles en la literatura y las aplicaciones relacionadas también han sido revisadas. Se han discutido las propiedades no lineales ópticas de nanopartículas de metales nobles y materiales compuestos, y sus aplicaciones para los activos ultra-rápidosplasmónicos, y el tratamiento médico. El artículo debe ser de gran utilidad para los nuevos investigadores que entran en este campo de estudio, y también para los expertos que participan en el diseño de los dispositivos basados en ONL.

Palabras clave: Óptica no lineal (ONL), propiedades ópticas no lineales de nanopartículas de Metales Nobles y aleaciones, plasmónica activa ultrarápida.

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I. INTRODUCTION

The nonlinear optics is different from the linear optics, in the sense that whereas the linear optics is the 'optics of weak light', in which the light is deflected or delayed but its frequency is unchanged, the nonlinear optics is the 'optics of intense light', in which we observe and study the effects induced by the light itself, as it propagates through the medium. The important breakthroughs connected with this field, made in the early 1960s are: (i) Discovery of Optical second harmonic generation, (ii) Discovery of Stimulated Raman scattering, and (iii) Stimulated Brillouin scattering, which is now used as an efficient technique for the generation / amplification of the coherent optical radiation with small frequency shift.

The understanding of the NLO concept can be done by starting from consideration of the meaning of the index of refraction (n). In the linear region, the electric field is much weaker than the intra-atomic field, and thus n is independent of the light intensity *(I)*. However, in case of the nonlinear region, the interaction of light in matter is studied, and it is found that it is possible to control n by the light itself, and also to manipulate one beam with the other, which in fact leads to many technical innovations. This nonlinearity is observed only at very high light intensities *i.e.* values of the electric field must be comparable to the inter-atomic electric fields, typically 10^8 V/m, and these are provided by pulsed lasers

The light wave acts differently on a molecule for the linear optics (LO) and nonlinear optics (NLO). In the first case, light wave acting on a molecule, vibrates it that in turn emits its own light wave, which then interferes with the original light wave. In the second case, the irradiance is high enough, resulting in the production of the vibrations at all frequencies corresponding to all energy differences between populated states. This difference in action is clearly understood by the following figure:

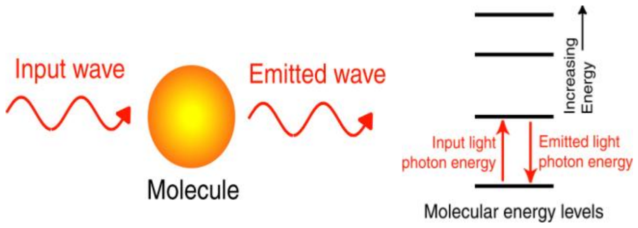

FIGURE 1a. Action of a light wave (linear optics) on a molecule.

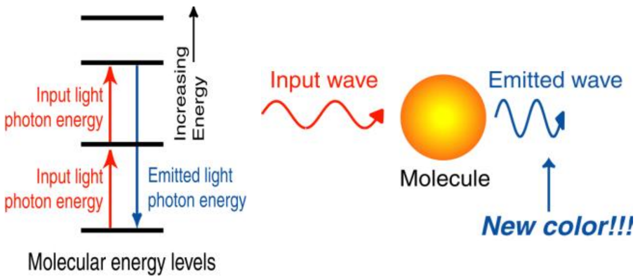

FIGURE 1b. Action of a light wave (linear optics) on a molecule. FIGURE courtesy M/s. Google.

This difference makes the NLO very important, which in fact, makes it possible to do the optical wave manipulation, which is one of the future technologies for optical processing. It may be noted that in case of the NLO, the refractive index, and thus the speed of light in a nonlinear optical medium is a function of the light intensity. Also, the well known principle superposition does not hold well in a nonlinear optical medium. In addition, the frequency of light is changed after it passes through a nonlinear optical medium; it can change its colour. Interestingly, photons interact inside a nonlinear optical medium, and thus the light can itself be used to control light. However, it should be well understood that the nonlinear (NL) optical behavior is not observed when light travels in free space, and displays itself only when it travels through the NL medium. The interaction of light with light results by the nonlinear medium, since the presence of an optical field modifies the properties of the medium, which causes another optical field, or even the original field itself. The NLO has many applications in fiber optics communications, and optoelectronics, which has resulted in making it an increasingly important topic in electrical engineering.

In studying the material response to light, we have to consider the induced polarization density P of the medium, which is given by:

$$P = \varepsilon_0 c(1)E + \varepsilon_0 c(2)E.E + \varepsilon_0 c(3)E.E.E$$

where ε_0 is the electric permittivity of free space, *E* is the electric field, and $c(i)$ is constant. The electric displacement *D* is given by:

$$D = \varepsilon_0 E + P + \varepsilon E \,.$$

It is important to note that the relation between *p* and *E* is linear when *E* is small, but becomes nonlinear when *E* has values comparable to interatomic electric fields, *i.e.* ~ 10^6 to 10^8 V/m. Another origin of a nonlinear response of an optical material to light, that is possible, is the dependence of the number density *N* on the optical field. Suppose that an optical field E_0 is incident on a nonlinear medium confined to some volume. This field creates a radiation source $S\langle E_0\rangle$, which radiates an optical field E_1, and in turn the corresponding radiation source $S\langle E_1\rangle$ radiates a field E_2, and so on, though only 2-3 terms are significant. In case of the linear optics, $n_2 + = 1 + c(1)$. However, in case of NLO, nonlinear terms have to be considered. If we consider the second order term *c*(2)*E.E*, we can understand the phenomena – frequency doubling, and sum and difference frequency generation. In case, we consider the third order term *c*(3)*E.E.E*, we can understand the third harmonic generation, and thus the phenomena like Raman scattering, Brillouin scattering, Self focusing, and Optical Phase Conjugation. We start our discussion by considering an optical beam with frequency ω and a DC field given by: $E=Eo + E\omega\cos(\omega t)$. In that case, we have to consider the term $c(2)EoE\omega\cos(\omega t)$, which leads to the linear electrooptic effect, called the Pockels effect, according to which n can be modified by applying a DC field, that, in fact can be used for optical switching and phase modulation of light. If we consider more terms *e.g.*, (i) $c(2)E\ \omega_2$, we find that a static voltage appears across the sample, (ii) $c(2)\ E_2\cos(2\omega t)$, and $c(3)\,E_0\,2E\omega\cos(\omega t)$, we observe the quadratic electro optic effect (DC Kerr effect), (iii) $c(2)E\,\omega_2\cos(2\omega t)$, which is equal to $c(3)\ E\,\omega_3\cos(3\omega t)$, we get the optical (AC Kerr effect). This explains that the refractive index depends on the optical field strength *i.e.*, $n = n_0 + n_2 I$, which leads to the phenomena - self-focusing and self-phase modulation.

The polarization produced in the two cases is respectively governed by the Equations (1) and (2), which are given below:

$$P = \varepsilon_0 \chi E \,, \tag{1}$$

and

$$P = \varepsilon_o[\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots], \qquad (2)$$

where P is the induced polarization of medium, and $\chi(i)$ is the susceptibility of the i-th order.

In case of the Two Wave Mixing, two beams of same frequency are combined to create a stationary interference pattern, which leads to the energy coupling between the two beams, and thus results in the beam amplification, due to the pumping of energy by one beam into the other.

The harmonic generation is of many types - like (i) Second harmonic generation (SHG), or frequency doubling, resulting in the generation of light with a doubled frequency, and hence half the wavelength, in which two photons are destroyed to create a single photon at two times the frequency; (ii) Third harmonic generation (THG), which results in the generation of light with a tripled frequency i.e. one-third the wavelength. and in this process, three photons are destroyed for creating a single photon at three times the frequency; and (iii) High harmonic generation (HHG), in which case, the generation of light with frequencies much greater than the original ~100 to 1000 times greater, takes place. NLO is a really very interesting concept, which has many associated phenomena - (i) Second harmonic generation, (ii) Sum frequency generation, (iii) Difference frequency generation, and (iv) the DC rectification. These are briefly explained mathematically below.

(i) SECOND HARMONIC GENERATION The Eq. (2) explains the effect of the nonlinear terms, as given below:

Since

$$E(t) \propto E_0 \exp(i\omega t) + E_0^*(-i\omega t),$$

hence

$$E(t)^2 \propto [\exp^2(2i\omega t) + 2|E_0|^2 + \exp^2(-2\omega t)]. \qquad (3)$$

This adds extra terms in the intensity of light, which leads to the formation of second order harmonic generation. Very commonly, this second harmonic generation is used to get the laser output at the frequencies, not easy to get otherwise *e.g.* a laser beam at 1064 nm, when passed through a second order nonlinear crystal, produces the laser output at twice the frequency, and hence at half the wavelength, which is 532 nm.

(ii) SUM AND DIFFERENCE FREQUENCY GENERATION. Let us consider the case, when there are two beams of different colors present at the same time in a nonlinear medium. The different colours have different wavelengths, and hence different frequencies ω_1 and ω_2. The Equation for the electric field is then given by:

$$\begin{aligned} E(t) \propto [&E_1 \exp(i\omega_1 t) + \\ &E_1^* \exp(-i\omega_1 t) + E_2(i\omega_2 t) + E_2^* \exp(-i\omega_2 t)]. \end{aligned} \qquad (4)$$

Hence, the intensity is given by the following equation:

$$\begin{aligned} E(t)^2 \propto\ &E_1{}^2.\exp(2\omega_1 t) + E_1 *^2 \exp(-2\omega_1 t) + E_2{}^2.\exp(2\omega_2 t) + \\ &E_2 *^2 \exp(-2\omega_2 t) + 2E_1E_2.\exp(i[\omega_1 + \omega_2]t) + \\ &2E_1^*E_2^*.\exp(-i[\omega_1 + \omega_2]t) + 2E_1E_2.\exp(i[\omega_1 - \omega_2]t) + \\ &2E_1^*E_2^*.\exp(-i[\omega_1 - \omega_2]t) + 2|E_1|^2 + 2|E_2|^2. \end{aligned} \qquad (5)$$

The terms in the various rows in the above Equation represent respectively the second harmonic generation, second harmonic generation, Sum-frequency generation, Difference- frequency generation, and the dc rectification.

II. MATERIALS USEFUL IN NLO

Many types of materials have been found useful for the NLO applications, each being suitable for a particular transmission range, and particular laser systems. LBO is useful in the 0.16-3.3mm transmission range, and finds applications in the High power lasers harmonics generation and OPO pumped by Nd:YAG harmonics. BBO is useful in the 0.19-3.3mm transmission range, and finds applications in the Solid State and Dye laser harmonics generation with output in the range 200-532 nm; - OPO/OPA pumped by Nd:YAG harmonics with 295-3000 nm output.KTP is useful in the 0.38-4.4 mm transmission range, and finds applications in the Harmonics generation in UV and VIS. KD*P is useful in the 0.26-1.6mm transmission range, and finds applications in the Harmonics generation in VIS range. LiNbO3 is useful in the 0.4-4.5 mm transmission range, and finds applications in the SHG and OPO pumped by Nd:YAG laser. LiIO3 is useful in the 0.3-6.0 mm transmission range, and finds applications in the SHG and THG of Nd:YAG, and DFM with output in 3-5 mm transmission range. AgGaS2 is useful in the 0.53-125 mm transmission range, and finds applications in the Harmonics generation and DFM with wide tunable output in 3-9 mm, IR visualization. AgGaSe2 is useful in the 0.73-18 mm transmission range, and finds applications in the SHG of CO2 lasers, OPO with 3-12 mm output. GaSe is useful in the 0.65-18mm transmission range, and finds applications in the SHG of CO and CO2 lasers, and DFM with output in 7-16 mm. CdSe is useful in the 0.75-25 mm transmission range, and finds applications in the DFM with tunable output up to 25 mm. AgAsS3 is useful in the 0.6-13 mm transmission range and finds applications in the IR visualization, DFM, and OPO. Te is useful in the 3.8-32 mm transmission range, and finds applications in the DFM with output in 15-30 mm.

In view of the growing importance and utility of the NLO, many useful studies [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] have recently been conducted on the materials, their synthesis and characterization, and other related aspects, which provide a deep insight into the subject.

III. APPLICATIONS OF NLO

There are numerous applications of the NLO in optics and optoelectronics. In fact, the NLO is responsible for bringing revolutionary progress in these fields. Some of the important applications are: (i) Optical phase conjugation, (ii) Optical parametric oscillators, (iii) Photorefractive effect, (iv) Self-focusing, (v) Optical solitons, and (vi) Optical computing. These are briefly discussed below:

(i) OPTICAL PHASE CONJUGATION (OPC) The Optical Phase Conjugation refers to the technique of generating a time-reversed replica of the wave, just like the action of the mirror. If there is an electric field $E = A\cos(\omega t\text{-}kz\text{-}f)$, then after phase conjugation, it becomes $Ec = A\cos(\omega t+kz+f)$, where both k and f are changed into negative, *i.e.* the time reversal of the wave takes place. Obviously, this technique has applications in processes like lensless imaging, and distortion correction, since they are associated with a frequency shift. The advantage of the NLO technique is that it can be done in real time.

In the generation of the Phase conjugate waves, four wave mixing (FWM) is used. Also, the case of the Degenerate Four Wave Mixing (DFWM) is similar to that of holography. It should be noted that the nondegenerate FWM, produces large frequency shift, which can be used for the stimulated scattering processes. However, the Brillouin scattering involves acoustic waves with small frequency shift. The case of Raman scattering is different in the sense that there are molecular vibrations or optical phonons with larger frequency shift.

The OPC technique is very useful for unraveling the distortions occurred in passing through a distorting medium. It is interesting to note that OPC takes place with the mixing of four waves of the same frequency. The waves 1 and 4 create an interference pattern, and thus produce an intensity dependent refractive index, which behaves like a phase grating, and finally, the wave 3 creates a phase conjugate of wave 2. For phase matching, the parameter wave vector k has to be equal to $-k$.

DFWM involves a third order nonlinear optical process, in which the grating induced by two input waves scatters the third wave, and thus generates the fourth wave. Interestingly, in this case, the inputs are two antiparallel, high power pumps, along with a weaker probe wave, which produce an output which is both amplified and conjugated. This technique differs from the conventional holography gratings, which are recorded in a photographic emulsion

Four Wave Mixing (FWM) is explained below:

In the case of three optical fields present in a nonlinear medium, mixing takes place, resulting in the creation of four waves, as shown in the figure 2.

Let us now discuss the Raman and Brillouin scattering processes mentioned above.

During the mixing of mechanical oscillations with a light beam in a nonlinear medium, there are mechanical variations *i.e.* variations of intra – atomic distance in a molecule, or variations of density in a solid or liquid. As a result, frequency spectrum of light is modified along with the emission or absorption of phonons. In case of the Brillouin scattering, the parameter n is a function of density, as this involves the Debye-Sears effect, which means that an acoustic wave scatters light with a Doppler shift. Therefore, the electronic polarization creates pressure variations. So in this case, light can pump a sound wave, and then can get scattered back with a slightly different frequency. Therefore, in case of the stimulated Brillouin scattering, interaction of photons with acoustic phonons takes place. The case of Raman scattering is also very interesting, in which the intraatomic distance in the molecule is changed, when the electron cloud is displaced. So this involves the vibration state of molecules. Also, in case of the Raman scattering, interaction of photons with optical phonons, takes place. The important difference between the two is that the variables in Raman scattering are microscopic, while in case of the Brillouin scattering, these are macroscopic.

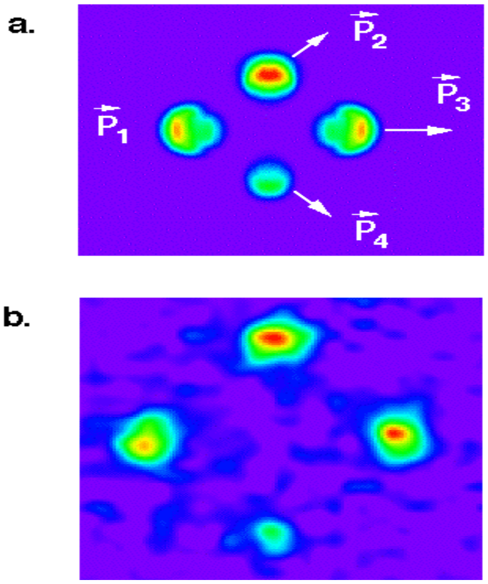

FIGURE 2. Four Wave mixing (FWM) – (a) and (b). Figure courtesy M/s. Google.

Imaging and Aberration correction using phase conjugate mirror (PCM) is very important for the case of the optical systems working in the turbulent media, and also for telescopic observations. For this imaging and aberration correction, the following setup is used:

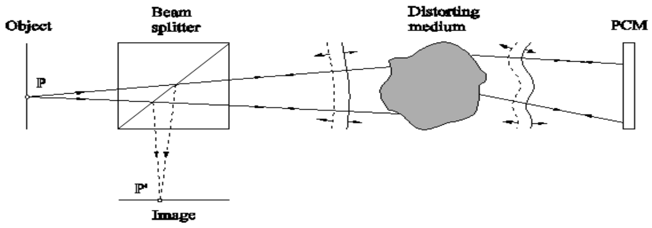

FiGURE 3. Basic two-pass schematic for imaging and aberration correction using a PCM.

The light from an object is incident on a beam splitter, and sends out a wavefront shown by the continuous line, which on passing through the distorting medium is distorted, as shown, and then is incident on the PCM. The reflected wavefront, after passing through the distorting medium restores the original wavefront and hence forms the corrected image in spit of the aberrations present in the medium. The image restoration can be done by the using the PCM. It has been observed that severely distorted laser beams can be corrected for the distortions produced after passing through the imperfect optics. The high power amplifiers are known for often distorting the laser beams, which makes them unsuitable for conducting the experiments. These distortions are corrected by double passing the amplifier using a PCM.

In some cases, the frequency of the conjugate wave taken is different from that of the signal wave. If we consider the pump waves are of frequency $\omega_1 = \omega_2 = \omega$, and the signal wave is of higher frequency, so that $\omega_3 = \omega + \Delta\omega$, then the conjugate wave produced is of frequency $\omega_4 = \omega - \Delta\omega$, and this is known as frequency flipping. The NLO can be used to exactly reverse the propagation direction and phase variation of a beam of light, and the reversed beam is called a conjugate beam, and therefore, this technique is called the optical phase conjugation. The process can also be looked as time reversal, wavefront reversal, and retroreflection of light.

It is very interesting to understand the three-wave-mixing process and from a photon-optics perspective as a process of three photon interaction, in which two photons of lower frequency, ω_1 and, ω_2 are annihilated, and a photon of higher frequency ω_3 is created. Sometimes, the reverse happens - the annihilation of a photon of high frequency ω_3 is accompanied by the creation of two low-frequency photons, of frequencies ω_1 and ω_2. It can be seen that $\hbar\omega$ and $\hbar k$ are respectively the energy and momentum of a photon of frequency ω and wave vector k, $\hbar$ being the reduced Planck's constant. Thus, the conservation of energy and momentum, in either case, requires that: $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$, and $\hbar k_1 + \hbar k_2 = \hbar k_3$, where k_1, k_2 and k_3 are the wave vectors of the three photons. These equations show that they represent the frequency matching and, the phase matching conditions.

(ii) OPTICAL PARAMETRIC OSCILLATORS (OPOs). It is really very interesting for the optical engineers to know that the OPC converts the pump wave into two coherent light waves, both with longer wavelengths. The schematic for this device is shown below:

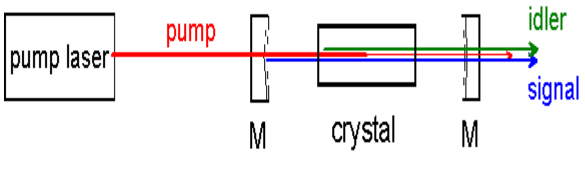

FIGURE4. Schematic of the Optical Parametric Oscillator.

The OPO consists of the NLO crystal placed between two mirrors, as shown in the figure. The OPC is able to convert the pump wave into two coherent light waves, both with longer wavelengths, and also shifted from the original path. One is called the 'idler' and the other the 'signal'. This is really very useful and handy for the researchers and scientists, as it has many applications including Light detection and ranging (LIDAR), High resolution spectroscopy, Medical research, Environmental monitoring, Display technology, and Precision frequency metrology.

(iii) PHOTOREFRACTIVE EFFECT. Photorefractive Effect is the phenomenon of a change of the local index of refraction due to the illumination of a beam with spatial variation of intensity, which is observed by passing the laser beams through electro optic crystals like - LiNbO3, BaTiO3, KNbO3, and LiTaO3. The Model for Photorefractive effect is very simple, and is based on the fact that there are impurities with energy levels around the middle of band gap *i.e.* donors. Obviously, the electrons get excited by the enough photon energy, which migrate and get trapped at nearby sites in the dark side. Due to the space charge separation, *E* field is affected, and this causes a change in the refractive index *n*. The photorefractive effect can create a periodic medium, and is associated with many important phenomena involving the scattering of light from gratings or holograms. Apart from the wave mixing, and phase conjugation, the NLO has applications in the dynamic holography. The medium having dielectric constant a periodic function of position acts like a grating.

The nonlinear optics technique is used to produce many exotic events, like – (i) changing the color of a light beam, and also changing its shape in space and time, (ii) switching telecommunications systems, and (iii) creating the shortest events *e.g.* transmitting IR radiation through a crystal yields the display of green light, as shown in the following figure:

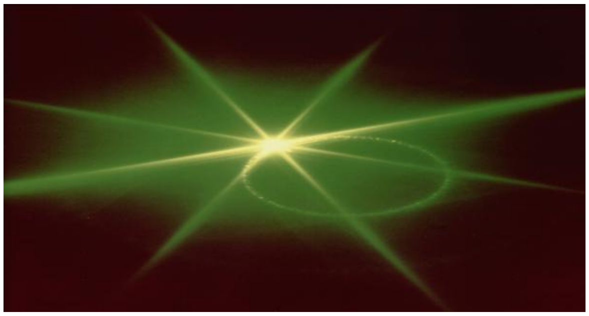

FIGURE 5. Display of green light by transmitting IR radiation through a crystal. FIGURE courtesy M/s. Google.

(iv) SELF-FOCUSING. Self-focusing is the phenomenon due to the Optical Kerr effect, and the higher order nonlinearities, which are caused by the spatial variation in the intensity, and hence create a spatial variation in the refractive index.

(v) OPTICAL SOLITONS. In the optical solitons, there is an equilibrium solution for either an optical pulse *i.e.*

temporal soliton or the spatial mode *i.e.* the spatial soliton, which does not change during propagation due to a balance between diffraction and the Kerr effect *e.g.* by self-phase modulation for temporal and self-focusing for spatial solitons.

(vi) OPTICAL COMUTING. The optical techniques can provide a number of ways of extending the information processing capability of electronics. In fact, it is now well understood that large quantities of data can be generated from different resources, and hence powerful computers are required to process them. For this type of work, the use of electronics is not sufficient, and therefore, it has to be augmented by the use the optics for providing the solutions. This has led to the fabrication of digital optical computer, which requires the use of nonlinear optics.

IV. NLO PROPERTIES OF NOBLE METAL NANOPARTICLES AND COMPOSITES

Recenty, a lot of work is going on for studying and using the NLO properties of Noble Metal Nanoparticles and Composites. The emphasis is on understanding and applying the nonlinear phenomena in bulk and nanosized metals. Cao and Brongersma [13] have suggested the use of Noble Metal Nanoparticles and Composites for faster and smaller data processing technology.

Let us first consider the linear optical properties, and discuss the permittivity of the metals (ε_m), which is given by the following equation:

$$\varepsilon_m = \varepsilon_{\mathrm{int}er} + \varepsilon_{\mathrm{int}ra}\,, \tag{6}$$

where εinter and ε intra are respectively the permittivities due to the interband and intraband transitions.

$$\varepsilon_{\mathrm{int}ra} = 1 - \frac{\omega_p{}^2}{\omega(\omega - i\gamma)}\,, \tag{7}$$

and

$$\varepsilon_{\mathrm{int}er} = 1 + \frac{\omega_p{}^2}{(\omega_0{}^2 - \omega^2) - i\gamma\omega}\,. \tag{8}$$

Where ω_p is the plasma frequency, τ is the mean free time between collisions *i.e.* electron-lattice collision time, γ is the damping constant, which in the quantum mechanical description, is replaced by $1/\tau$.

Papadopoulos *et al*. [14] have studied the variation of the mod of Fermi distribution function f ωrtλ (nm) in the visible region for the cases of Ag: vacuum, Au:Al2O3, Ah:SiO2, and Au: vacuum. Their results are quite interesting, and have been reproduced below.

It is observed that whereas, the first case shows the maximum in the UV region, the other three show the distinct maxima in the visible region, with the different amplitudes, and at different wavelengths though quite close to each other.

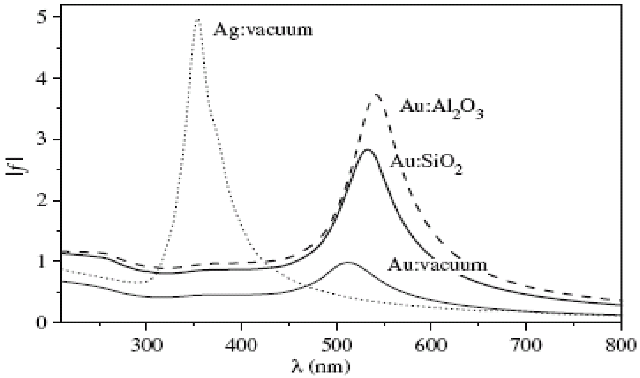

FIGURE 6. Variation of amplitude of fwrtλ (nm). FIGURE courtesy Papadopoulos M. G., Sadlej A. J. and Leszczynski J., Non-Linear Optical Properties of Matter—From Molecules to Condensed Phases, (Springer, Dordrecht, The Netherlands, 2006).

After including the terms for NLO effect, these equations are modified as below:

$$P = \varepsilon_0[\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots]\,, \tag{9}$$

$$P^{(3)}(\omega) = 3\varepsilon_0\chi^{(3)}(\omega)\left|E(\omega)\right|^2 E(\omega)\,, \tag{10}$$

for the Optical Kerr Effect, and

$$P^{(3)}(3\omega) = \varepsilon_0\chi^{(3)}3(\omega)E^3(\omega)\,, \tag{11}$$

for the Third Harmonic Generation (THG). The refractive index *n* and the molecular polarizability α are modified as

$$n = n_0 + n_2 I\,, \tag{12}$$

and

$$\alpha = \alpha_0 + \alpha_2 I\,. \tag{13}$$

Where α = *(dipole moment* μ*/ local field)*. So the values of the $\chi^{(i)}$ for the real and imaginary parts are respectively given by:

$$\mathrm{Re}\,al\,\chi^{(3)} = (4/3)\varepsilon_0 c n_0{}^2 n_2\,, \tag{14}$$

and

$$\mathrm{Im}\,aginary\,\chi^{(3)} = (2/3k)\varepsilon_0 c n_0{}^2 \alpha_2\,. \tag{15}$$

(i) NLO PROPERTIES OF THE NANOPARTICLES (NPs), POLYMERS, AND LIQUIDS. There are many types of NPs like – CdSSe in glass, Gold in glass, polymers like – polydiacatylenes (PTS, BCMU), and liquids like – Acetone, Benzene, Ethanole, Methanol. They have refractive index no, χ(3) in esu, and n_2 in cm^2/W respectively in the ranges 1.5 – 1.7, 1.5 x 10 to the power minus 8 – 8.0 x 10 to the power minus 14, and 2 x 10 to the power minus 10 – 8 x 10 to the power minus 16. Some of them (PTS and 4BCMU) have even negative values of χ(3) in esu, and n_2 in cm^2/W. There are also NPs of crystals like – CdS, GaAs, and ZnSe, and glasses like – Fused Silica, BK7, and As2S3 glass having these values in the ranges 1.4 –2.48, 1.0x 10 to the power minus 10 –4.4x 10 to the power minus 15, and 3.3 x 10 to the power minus 13 – 9.0 x 10 to the power minus 17. The NLO engineers choose the particular material according to the requirement and specifications. Sometimes, the results are not completely in agreement with the theoretically predicted values, and hence after the feedback, the corrections are applied to achieve the optimized results.

Voisin *et al*. [15] have studied the NLO properties of such materials, by investigating the ultrafast electron-electron scattering and energy exchanges in noble-metal nanoparticles. They have investigated the conduction electron energy exchanges in gold and silver nanoparticles with average size in the range from 2 to 26 nm, embedded in different matrices, and also have performed the experimental studies by following the internal thermalization dynamics of photoexcited nonequilibrium electrons with a femtosecond pump probe technique. It has been observed in both the metals, that the measured electron thermalization times are close to the bulk ones for nanoparticles larger than 10 nm, but interestingly are sharply decreasing for smaller ones. Their results show an increase of the efficiency of the electron-electron energy exchanges in small nanoparticles. It has now been established that the origin of intrinsic nonlinearity is due to the thermal and electronic contribution, and also we have to notice the size dependencies.

Recently, noble metals have been finding many applications in the nonlinear optics. In case of the noble metals, the *d*-bandsof the electronic structure are filled. Based on this definition, only copper, silver and gold are noble metals, as all *d*-like bands are filled and do not cross the Fermi level. Band structure of the noble metals is shown below:

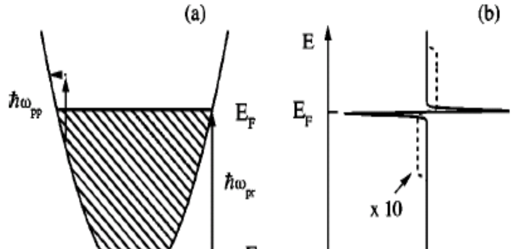

FIGURE 7. Band structure of noble metals. Ed and EF, shown in this FIGURE represent the energies corresponding to the d bands, and the Fermi level.

Takeda *et al*. [16] have measured the variation in *ε* of the effective medium, and the variation in intrinsic *ε* of the metal nanoparticles. Takeda *et al*. [17] have experimentally evaluated the optical nonlinearity of Cu nanoparticle materials by measuring the transient optical spectra employing the pump-probe method. Also, they have analysed the wavelength dispersions of nonlinear dielectric function on the hot electron contribution using the Maxwell Garnett model with the Drude model for intraband transition and the first principles calculation for interband transition. It has been emphasized that the evaluated dispersion does not directly reflect the local field factor. Some important observations have been made: (i) The experimental dispersions are quite consistent with the calculated values based on hot electron contribution; (ii) The interband transition term in hot electron contribution dominates the dispersion, and attains the lower photon energy beyond the absorption edge, and (iii) The intrinsic interband contribution is not negligible. It has been observed that there are well defined peaks for all the cases – interband term, intraband term, and the total term, both on the positive side and negative side, in the photon energy band from 1.6 eV to 2.6 eV. The variations in ε' and ε'' are such that in general, when one is positive, the other is negative. The modulus of the interband curve peaks is larger than that of the interband curve peaks. Of course, as expected, the modulus of the total term curve peaks is much larger.

V. SOME IMPORTANT APPLICATIONS OF THE NLO

Though, the NLO has many applications for research in the physical and medical sciences, some of the important ones are discussed here. One of the most important ones is the use of the gold nanoparticles (NPs) for photothermal therapy in treating cancer. Huang *et al.* [18] have shown the potential use of the enhanced nonlinear properties of gold nanospheres in photothermal cancer therapy by applying this technique based on the SHM, and using 800nm excitation, which is transparent to skin. It has been observed that this technique requires ~ 20 times lower energy to destroy cancer cells, as compared to the earlier techniques, and hence does not have serious harmful sideeffects. Three types of cases - NPs in solution, NPsIgG in solution, and NPsIgG on cell, have been investigated, and the variation of the optical density with wavelength in the 450nm – 800nm have been studied (Figure 8a). The peak optical density equal to unity is available in the 500 nm – 550 nm range in each case. The technique has been found to be useful in treating cancer cells (Figure 8b). These results have been reproduced below.

The other important application is for All-optical switching in subwavelength metallic grating structure containing Au:SiO_2 composite material, which is based on the optical Kerr effect. Min *et al.* [19] have proposed and numerically investigated the all-optical switching based on a subwavelength metallic grating structure containing nonlinear optical materials. They have used the metal-dielectric composite material in the switching for its larger third-order nonlinear susceptibility (~10−7esu) and the ultrafast response properties. It has been observed that the calculated dependence of the signal light intensity on the pump light intensity has a bistable behavior, which results in a significant switch effect. The study of this switching structure has established many novel advantages like - smaller size, requirement of lower pump light intensity, and shorter switching time ~ picosecond level.

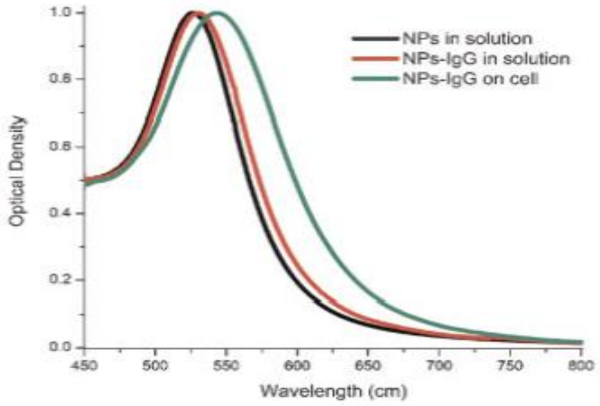

FIGURE 8a. Variation of the optical density with wavelength for the NPs.

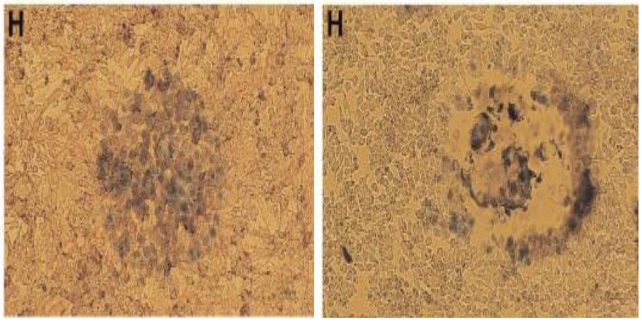

FIGURE 8b. Photothermal cancer therapy using gold nanoparticles. Figure courtesy Huang X., Qian W., El-Sayed I. H., and El-Sayed M. A., Lasers in Surgery and Medicine, **39**,747 – 753 (2007).

The experimental arrangement and the switching in subwavelength metallic grating structure, have respectively been shown in the Figures 9a and 9b. The variation of signal transmission with time (ps) and wavelength (nm), and the variation of transmission with wavelenth (nm) have respectively been shown in the LHS and the RHS of the Figure 9c.

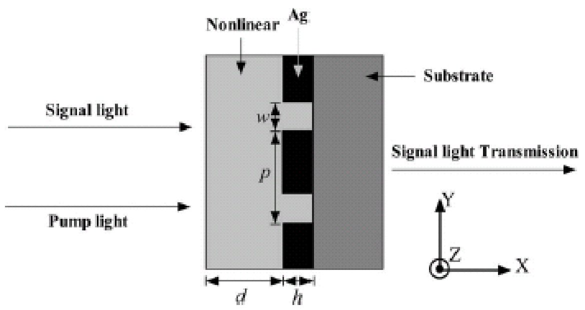

FIGURE 9a. Schematic of the subwavelength metallic grating structure.

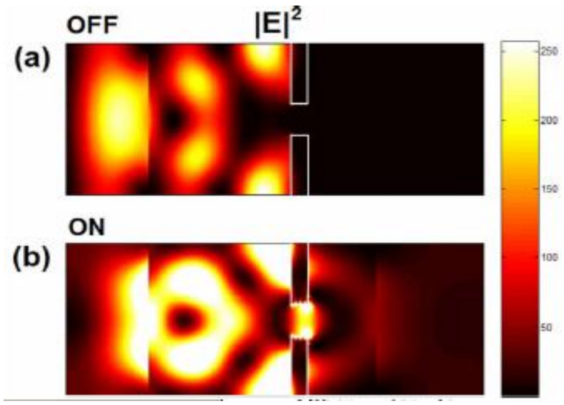

FIGURE 9b. llustration of the ‘All-optical switching’.

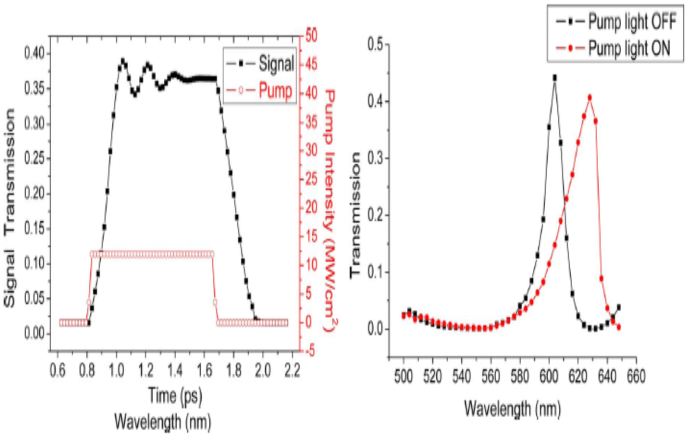

FIGURE 9c. The variation of signal transmission with time (ps) and wavelength (nm) –left; and the variation of transmission with wavelenth (nm) –right. FIGURE courtesy Min C., Wang P., Chen C., Deng Y., Lu Y., Ming H., Ning T., Zhou Y., and Yang G., Opt. Lett. **33**, 869-871 (2008).

It is observed that the signal transmission increases more than three times, and the transmission peaks are slightly shifted (~35nm) ωrt the other. Also, the peak value is slightly reduced (by ~ 15%) in pump light on position from that in the pump light off position. These observations are really crucial for the all-optical switching.

There is an increasing need for faster and smaller data processing technology, and understanding nonlinear phenomenon in bulk and nanosized metals. The concept of the “Ultra-fast active plasmonics” has been explained recently by MacDonald *et al.* [20], who have reported the results of their investigations on (i) the dependece of optical conductivity on energy, (ii) the dependece of SPP signal modulation (a.u.) on the pump-probe delay (ps), and (iii) the variation of the SPP signal modulation on the pump fluence (mJ/cm2). They have emphasized that the surface plasmonpolaritons, propagating bound oscillations of electrons and light at a metal surface, have great potential as information carriers for the highly integrated nanophotonic devices of the next generation. They have reported that the femtosecond optical frequency plasmon pulses can propagate along a metal–dielectric waveguide, and that they can be modulated on the femtosecond timescale by direct ultrafast optical excitation of the metal, and hence have concluded that it is possible to have terahertz modulation bandwidth, which is an astonishingly great speed - at least five orders of magnitude faster than the earlier existing technologies.

The curves of the dependence of the signal SPP modulation on the pump-probe delay, display well defined peaks centred at zero pump probe delay, and have been reproduced in the figure given below:
The variation of the signal SPP modulation with the pump fluence (mJ/cm2) for the fast component and the slow component are observed to be of the similar form, but in the ratio (the fast component to the slow component) of 2 or more at each value of the pump fluence. Caspers *et al.* [21] have extended this work by studying the silicon based ultrafast active plasmonics near the 1.5 μm wavelength.

VI. CONCLUSIONS

On the basis of the research work carried out so far on the NLO, it has been established that the noble metals are promising candidates for nonlinear optics, ultra-fast active plasmonics, and medical therapy applications. The NLO designers consider their size, surrounding medium and excitation characteristics so as to engineer them to have optimum desired response. Research work is progressing for providing further insight to quantum metallic systems, by using ultrashort high power pulses, and the nonequilibrium electron distribution studies. Recently, Cai *et al.* [22] have done a remarkable study, and have shown the electrically controlled nonlinear generation of light with plasmonics, which is expected to be of great use in many plasmonics based NLO devices.

Serious efforts are expected to be made in various other fields like - Optical Computing, Fourier Optics using FWM, Image Subtraction, Optical Interconnection, Amplification, Dispersion cancellation, Optical switches with dynamic holography (1 ms recording time). Optics has an important role to play in optical computing *e.g.* digital optical computers, based on the NLO technology. Some newer ideas and applications in nonlinear optics have been reported [23, 24, 25, 26, 27, 28, 29, 30, 31] during the last decade. Soljacič and Joannopoulos [23] have investigated and discussed in detail the enhancement of nonlinear effects using photonic crystals. Cowan and Young have [24] suggested a good technique of the mode matching for second-harmonic generation in photonic crystal waveguides. Mookherjea and Yariv [25] have shown the second-harmonic generation with pulses in a coupled-resonator optical waveguide. Sun *et al.* [26] have given a very novel idea of the photonic nonlinearities via Quantum Zeno blockade**.** Soljacič *et al.* [27] have provided a technique of the photonic crystal slow light enhancement of nonlinear phase sensitivity. Soljacič *et al.* [28] have been able to show the optimal bistable switching in nonlinear photonic crystals. Xu *et al.* [29] have done a detailed Quantum analysis and the classical analysis of spontaneous emission in a microcavity. Payam et al. [6] have analysed the Type-0 second order nonlinear interaction in monolithic waveguides of isotropic semiconductors. Another important study has been made by Yanik*et al.* [30], who have established the high contrast all-optical bistable switching in photonic crystal microcavities.

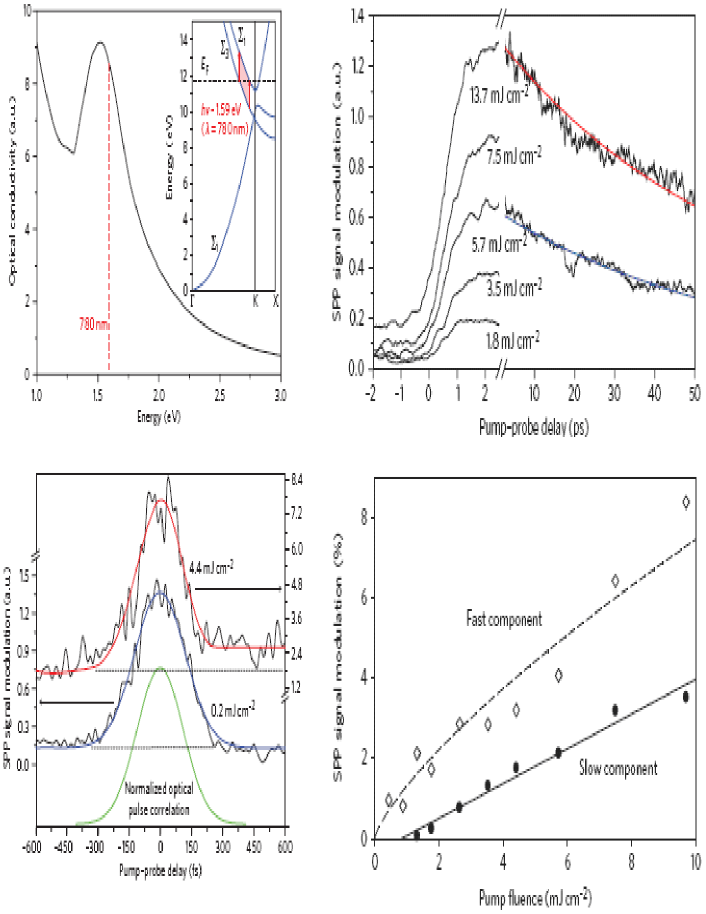

FIGURE 10. The curves of the dependence of the signal SPP modulation on the pump-probe delay, display well defined peaks centred at zero pump probe delay. FIGURE courtesy MacDonald, K. F., Sámson, Z. L., Stockman, M. I. and Zheludev, N. I. Nature Photon. **3**, 55–58 (2009).

Optical Techniques associated with the NLO, provide many ways of extending the information processing capability of electronics, because of the fact that huge quantities of data can be generated from different resources, which require a powerful computer for processing them. Some solutions in this direction can be obtained not by electronics alone, and hence, the NLO systems are very usefully employed in these cases. Some of the commonly used materials for the NLO applications are - GaSe, CdSe, AgAsS3, and LiIO3with transmissions in the different regions and having utility for different applications. Efforts are being made to find newer elements and also to improve the performance of the devices based on these materials.

Though the topic of Nonlinear Optics at preset has grown into a vast and active field with a lot of potential for technological applications, the NLO materials capable of giving the optimized components, have still to be realized in practice. The organic nonlinear optical materials are expected to play an important role in the future applications of the NLO. Various new nonlinear optical materials and devices have been developed, but are still in the infancy stage, and efforts are being made to improve their performance. Research efforts are focused on realizing the efficient purely optical information processing systems. Thus, it can be safely concluded that the topic of the NLO is on a firm footing, and expected to be used in the newer and important applications.

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