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NANOMATERIALS FOR NONLINEAR OPTICAL (NLO) APPLICATIONS: A REVIEW

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Abstract. Nonlinear optics is given increasing attention due to its wide application in the area of laser technology, optical communication and data storage technology .The growth of activities on NLO properties of nanomaterials, proposed by the agitation of understanding new science and potential hope for applications in daily life as optical devices, photonic circuits, and environmental sensor as well as in medical diagnostics. Intense research has been fueled by the need for practical optical device that can deal the deficiencies of conventional technologies. The leading materials could have very high bulk second order NLO values well beyond those available today, which in turn would enable optical switches and modulators of smaller dimensions than what is currently available, while at the same time substantially reducing the cost of fabrication of electro-optic (EO) devices.This paper mainly focus on recent advances in second and third order NLO properties of nanomaterials and understanding new science behind the extraordinary NLO values of nanomaterials. It also discusses about the development of nanomaterial based optical technology.

1. INTRODUCTION

Nonlinear optics, which studies the interaction of intense light field with matter, is a relatively new field in physics with lots of fundamental scientific and technological potential applications [1-3]. Non linear optical (NLO) effects are analyzed by considering the response of the dielectric material at the atomic level to the electric fields of an intense light beam. The propagation of a wave through a material produces changes in the spatial and temporal distribution of electrical charges as the electrons and atoms interact with the electromagnetic fields of the wave. The main effect of the forces exerted by the field on the charged particles is displacement of the valence electrons from their normal orbits. This perturbation creates electric dipoles whose macroscopic manifestation is the polarization. Thus nonlinear Optics (NLO) is the study of interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude. Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The light propagated through a crystalline solid, which lacks a center of symmetry, generates light at second and higher harmonics of the applied frequency. Such frequency doubling processes are commonly used to 33 produce green light (532 nm) from, for example, a Nd: YAG (yttrium-aluminium-garnet) laser operating at 1064 nm. This important nonlinear property of noncentrosymmetric crystals is called second harmonic generation.

Following the rapid development of nanotechnology in the past few decades, a large number of nanomaterials have been shown to possess remarkable NLO properties, which motivates the design and fabrication of nano and

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nano-scale photonic and photoelectronic devices [4].The most products of nanotechnology as examples are carbon-based nanomaterials: from 3D carbon black or nanoparticles [5,6] to 0D fullerenes [7,8] to 1D carbon nanotubes (CNTs) [9–12] and then to 2D graphenes [13,14] discovered most recently. In addition to the outstanding mechanical, electrical and thermal properties [15-18], the unique NLO properties of CNTs have generated much research interest from both experimental and theoretical aspects [19–21]. The Z-scan is a simple but powerful technique to characterize the NLO properties of materials, including nonlinear absorption, scattering or refraction [22]. In this method a laser beam is focused by a convex lens to create an intensity-spatially-varied optical field. When an optical material is moved around the focal point along the z-axis, one can readily obtain information on the variation of transmission against incident intensity, and hence the nonlinear parameters of interest. The present paper, summarize and evaluate the achievements in the development of second and third order NLO nanomaterials.

2. SURVEY OF NONLINEAR OPTICS

The development of nonlinear optical (NLO) materials has been driven by a multitude of important technological applications that can be accomplished if suitable materials are available [23–26]. Future generations of optoelectronic devices for telecommunications, information storage, optical switching, and signal processing are predicted to a large degree on the development of materials with exceptional NLO responses. A large number of organic π-conjugated molecules have been investigated in the last thirty years for suitability to function as components in hypothetical NLO materials [27-32]. Second-harmonic generation (SHG) was first observed in a single crystal of quartz by Franken *et al.* [33]. Parametric amplification was observed in lithium niobate ($LiNbO_3$) by two-wave mixing in temperaturetuned single crystals [34]. Rentzepis and Pao [35] made the first observation of SHG in an organic material, benzpyrene, in 1964. Heilmeir [36] examined hexamethylenetetramine single crystal SHG in the same year [37]. Two other organic materials followed rapidly: hippuric acid and benzil [38]. Benzil was the first material that proved relatively easy to grow into large single crystals. Over the last two decades the study of nonlinear optical process in organic and polymer systems has enjoyed rapid and sustained growth [23-38].

The rapid growth of the field is mainly due to the technological promise of these materials. Traditionally, the materials used to measure second-order NLO behavior were inorganic crystals, such as lithium niobate ($LiNbO_3$) and potassium dihydrogen phosphate (KDP). The optical nonlinearity in these materials is to a large extent caused by the nuclear displacement in an applied electric field, and to a smaller extent by the movement of the electrons. This limits the bandwidth of the modulator. Organic materials have a number of advantages over inorganic materials for NLO applications [39-48]. At the molecular level, they need to be non-centrosymmetric. A large number of organic π-conjugated molecules have been investigated [39-46] in the last twenty years. The outcome of the results has helped to establish certain guidelines for molecular design to get good second order NLO materials. However, roughly more than 80% of all π-conjugated organic molecules crystallize in centro-symmetric space groups, therefore producing materials with no second order bulk susceptibility. To overcome this limitation, organic NLO material doped or covalently attached in polymers, have been introduced by Dalton *et al.* [49]. A few of these chromophores have served as components of functioning polymer-based optoelectronic devices; the physical properties of all these prototype materials possess one or more critical deficiencies that render commercialization of these systems impractical [25-31]. The ability to integrate metal nanoparticles into biological systems has greatest impact in biology and biomedicine [50-73]. Development of nanobased biosensors has increased tremendously over the past few years as demonstrated by the large number of scientific publications in this area. The emerging ability to control the patterns of matter on the nanometer length scale can be expected to lead to entirely new types of biological sensors [74-84]. These new systems will be capable of sensing at the single-molecule level in living cells, and capable of parallel integration for the detection of multiple signals, enabling a diversity of simultaneous experiments, as well as better crosschecks and controls.

3. THEORY OF NONLINEAR OPTICS

When the electromagnetic field of a laser beam is acting on an atom or a molecule, it induces electric polarization, which gives rise to many of the unusual and interesting properties that are optically nonlinear. In a dielectric material, the influence of an electric field causes distortion in the spatial distribution

between the electrons and the nucleus. These distortions cause electric dipoles, which in-turn manifest as polarization. At very low fields, the induced polarization is directly proportional to the electric field. However, at intense electric fields, polarization becomes independent of the field and the susceptibility becomes field dependent. The induced polarization is capable of multiplying the fundamental frequency to second, third order and even higher harmonics. The irradiation from the oscillating dipoles differs in amplitude with respect to the incident sinusoidal electric field. As a consequence, the distorted reradiated waves contain different frequencies from that of the incident wave. When the electric field associated with the radiation is small, the induced polarization is given by

$$\vec{P} = \varepsilon_0 \chi^{(1)} \vec{E}, \tag{1}$$

where $\vec{P}$ is the polarization vector, $\vec{E}$ is the electric field vector, $\chi^{(1)}$ is the linear susceptibility, and ε_0 is the permittivity of free space. When the optical electric field strength is very high and comparable to the intra-atomic electric field, the induced polarization is given by

$$\vec{P} = \varepsilon_0 \chi^{(1)}.\vec{E} + \chi^{(2)}.\vec{E}.\vec{E} + \chi^{(3)}.\vec{E}.\vec{E}.\vec{E} + \ldots, \tag{2}$$

where $\chi^{(2)}$, $\chi^{(3)}$ …. are the nonlinear susceptibilities of the medium.

The nonlinear susceptibilities have decreasing magnitudes as their order increases at $\chi^{(1)}$: $\chi^{(2)}$: $\chi^{(3)} \approx$ 1:10^{-8}: 10^{-16}. The first order susceptibility which is the linear term, $\chi^{(1)}$, gives rise to refractive index, absorption, dispersion and birefringence of the medium. The second order, $\chi^{(2)}$, gives rise to Second Harmonic Generation (SHG), frequency mixing and parametric generation, while the third order nonlinear susceptibility, $\chi^{(3)}$,gives rise to third harmonic generation, stimulated Raman scattering, optical bistability and conjugation. Supposing that we want to study the interaction of two travelling waves

$$\vec{E}_1(z,t) = \vec{E}_1 \cos\left(\omega_1 t + k_1 z\right), \tag{3}$$

$$\vec{E}_2(z,t) = \vec{E}_2 \cos\left(\omega_2 t + k_2 z\right). \tag{4}$$

Considering the second order nonlinearity in polarization alone

$$\vec{P} = \chi^{(2)} \vec{E}^2, \tag{5}$$

$$\vec{P} = \chi^{(2)} \left[\vec{E}_1^2 \cos^2\left(\omega_1 t + k_1 z\right) + \vec{E}_2^2 \cos^2\left(\omega_2 t + k_2 z\right) + 2\vec{E}_1 \vec{E}_2 \cos\left(\omega_1 t + k_1 z\right) \cos\left(\omega_2 t + k_2 z\right) \right]. \tag{6}$$

It can be found that the polarization consists of a number of components with different frequencies viz.,

$$\vec{P}_{1\omega_1} = \chi^{(2)} \vec{E}_1^{\,2} \cos\left[2\left(\omega_1 t + k_1 z\right)\right], \tag{7}$$

$$\vec{P}_{2\omega_2} = \chi^{(2)} \vec{E}_2^{\,2} \cos\left[2\left(\omega_2 t + k_2 z\right)\right], \tag{8}$$

$$\vec{P}_1\omega_1 + \vec{P}_2\omega_2 = \chi^{(2)} \vec{E}_1 \vec{E}_2 \cdot \cos\left[\left(\omega_1 + \omega_2\right)t + \left(k_1 + k_2\right)z\right], \tag{9}$$

$$\vec{P}_1\omega_1 - \vec{P}_2\omega_2 = \chi^{(2)} \vec{E}_1 \vec{E}_2 \cdot \cos\left[\left(\omega_1 - \omega_2\right)t + \left(k_1 - k_2\right)z\right], \tag{10}$$

and a steady term

$$\vec{P}_{direct} = \left(\frac{\chi^{(2)}}{2}\right)\left(\vec{E}_1^2 + \vec{E}_2^2\right). \tag{11}$$

The different components of nonlinear polarization generate electromagnetic waves having frequencies different from those of the incident waves. Fraction of the incident energy used to create nonlinear polarization can be reradiated at one or more number of different frequencies.

By employing proper phase matching conditions it is possible to generate any one of these components of the polarization wave with high efficiency.

$$k_1 + k_2 = k_3$$

$$\text{(Or)} \quad \frac{n_1\omega_1}{c} + \frac{n_2\omega_2}{c} = \frac{n_3\omega_3}{c}. \tag{12}$$

Franken *et al*. (1961) observed the frequency doubling for the first time, by irradiating a quartz crystal with a ruby laser beam that operated at 694.2 nm. A very small amount of the light striking the crystal was converted into a light with a wavelength of 347.1 nm. This wavelength lies in the ultraviolet region of the spectrum and is exactly half the wavelength and twice the frequency of the incident laser light. For efficient energy transfer, the two waves should remain in phase i.e., $n_1 = n_2$. Due to normal dispersion occurring in the materials in the optical region, the radiation will generally lag behind the polarization wave. The phase mismatch between the polarization and electromagnetic wave is given by

$$\Delta k = \left(\frac{4\pi}{\lambda}\right). \tag{13}$$

For improving the efficiency of the doubled frequency, the crystal has to be phase matched .The dispersion in the materials can be offset by using the natural birefringence. There exist two indices of refraction for a given direction of propagation, corresponding to the two allocated orthogonally polarized modes. By an appropriate choice of polarization and direction of propagation, it is often possible to obtain phase matching or index matching, where $\Delta k = 0$. To realize the nonlinear effect, a suitable medium is required. The conversion efficiency, η_{SHG} defined as the ratio of the emerging second harmonic power $P_{2\omega}$ to the incident power P_{ω} is one of the most useful measures of the performance of a nonlinear crystal. It is represented by

$$\eta = \frac{P_{2\omega}}{P_{\omega}} = 2\left[\frac{\mu_0}{\varepsilon_0}\right]^{3/2} \frac{\omega^2 d^2 l^2 \sin\left[\frac{\Delta k l}{2}\right]}{n^3\left[\frac{\Delta k l}{2}\right]^2}\frac{P_{\omega}}{A}, \qquad (14)$$

where $\Delta k = k_{2\omega} - 2k_{\omega}$,
$k = 2\pi/\lambda$,
ε_0 = permittivity of free space,
μ_0 = permeability of free space,
n = index of refraction,
ω = angular frequency of incident light,
l = length of the crystal,
A = beam area.

The factor Δk represents the amount of phase mismatch between the second harmonic wave fronts generated at different points in the crystal. If Δk is zero (proper phase matching) then the interference term,

$$\frac{\sin^2\left[\frac{\Delta k l}{2}\right]}{\left[\frac{\Delta k l}{2}\right]^2} = 1 \qquad (15)$$

reaches a maximum value that in-turn maximizes the efficiency of the SHG process. The efficiency of second harmonic generation is directly proportional to the intensity $I(\omega)=P_{\omega}/A$ of the incident fundamental radiation.

4. NON-LINEAR OPTICAL GENERATION

The nanomaterials with particle size or film thickness much small than the coherent length, the phase matching condition is usually neglected and the surface nonlinearity makes a apparent contribution due to the enhanced surface to volume ratio. Surface second harmonic generation (SHG) from metals was established on the existence of the nonlinear $E(\nabla E)$source term that has a large contribution at the boundary due to the discontinuity of the lattice structure and the presence of the bulk magnetic dipole term $E \times \partial H/\partial t$ arising from Lorentz force of electrons. Accordingly the theory of SHG from metal surface was built up and modified by the phenomenological parameters *(a,b)*which, respectively, express the components of current density that are normal and parallel to the surface as proposed by Rudnick and Stern [85]. However, the discussion of azimuthally scanned SHG depending on the interface relation of metal films and the formation of nanoparticles on silicon substrate is still rarely discussed [86].For metal particles with structure of inversion symmetry, the electric quadruple field within the selvedge region is the dominant source for the generation of second harmonic light [87-88]. The excitation of surface plasmon (SP), which couples the incident field to propagate along the surface, is thus a main strategy for the enhancement of second harmonic generation (SHG). The efficiency of generating surface plasmon depends on the momentum conservation of the electromagnetic waves, which has a rather narrow bandwidth of wave-vectors. The random orientation of the scattered light of the innumerable nanoparticles pursues the phase matching condition. Recently, a significant growth of the intensity of the second harmonic generation (SHG) reflected from metallic island films [89-91] have been reported. The enhancement of the SHG of small metallic particles can be clarified by evaluating, quantum mechanically, the quadrupole susceptibility with the exploiting of quantum sphere model [92]. The current source $J(2\omega)$ for the SHG in the S direction is related to the polarization $P(2\omega)$ by

$$J(2\omega) = \frac{\partial P(2\omega)}{\partial t} = -2i\omega P(2\omega). \qquad (16)$$

We can write the second harmonic polarization by

$$P_{\alpha}(2\omega) = \frac{1}{2i\omega}\Delta_{\alpha\beta\gamma\delta} E^{\omega}_{\beta}\nabla_{\gamma}E^{\omega}_{\delta} = \chi^{Q}_{\alpha\beta\gamma\delta}E^{\omega}_{\beta}\nabla_{\gamma}E^{\omega}_{\delta}, \qquad (17)$$

where $\chi^{Q}_{\alpha\beta\gamma\delta} = (1/(2i\omega)\Delta_{\alpha\beta\gamma\delta})$ is the electric quadrupole, which can be evaluated quantum mechanically. Only the electrons at states near the Fermi energy can contribute to quadruple transition. Atedious calculation with isotropic average of the polarization

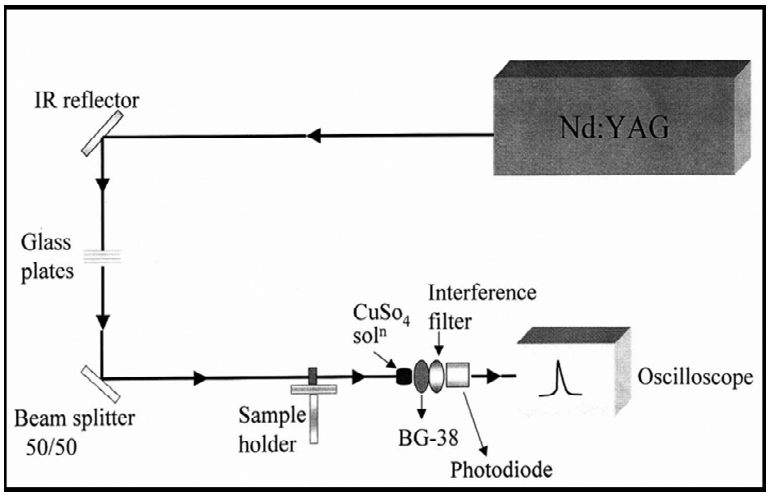

Fig. 1. Schematic experimental setup for SHG efficiency measurement.

directions implies the values of electric quadrupole as given by

$$\chi^{Q}_{\alpha\beta\gamma\delta} = \left[\frac{16A_{\alpha\beta\gamma\delta}e^3\eta E_F^{5/2}}{\sqrt{2}\pi^4\sqrt{m}(\eta\omega)^5}\sum_{k}^{k\max}\frac{1}{(2k+1)^2}\right] + \frac{1}{R}\left[\frac{24A_{\alpha\beta\gamma\delta}e^3\eta E_F^{2}}{\pi^3 m(\eta\omega)^5}\sum_{k}^{k\max}\frac{1}{(2k+1)^2}\right] + \frac{1}{R^2}\left[\frac{16A_{\alpha\beta\gamma\delta}e^3\eta E_F^{3/2}}{\pi^3 m(\eta\omega)^5}\ldots\right], \quad (18)$$

whereis $A_{\alpha\beta\gamma\delta} = P\,\Sigma_{nks}\theta^{nk}_{\alpha}\theta^{ks}_{\beta}\Omega^{sn}_{\gamma\delta}$ the total average value of the angular distribution in the $\alpha\beta\gamma\delta$ tensor components, θ^{nk}_{α} and $\Omega^{nk}_{\alpha\beta}$ are values of the angular distribution of p^{nk} in the a direction and Q^{nk} in the abdirection respectively and P is the permutation operator of $\alpha\beta\gamma\delta$. The $\chi^{Q}_{\alpha\beta\gamma\delta}$ contains three terms which are independent, inverse linear dependent, and inverse quadratic dependent on the particle radius, respectively. The second and third terms of above equation clearly adduces the enhancement of the quadrupole susceptibilityas the particle size R reduces.

4.1. Second harmonic generation (SHG)

The Second harmonic generation **(**SHG) is a special case of sum frequency generation, in which photons (ω_1) interact with the NLO media and are converted into new photonswith twice the energy ($2\omega_1$). As a second order NLO process, onlynon-centrosymmetric structures are able to emit SHG signals. Strong SHG signals have been found in many types of single inorganic nanostructures, including ZnO nanowires [93], GaN nanowires [94], $KNbO_3$ nanowires [95], noble metallic nanoparticles [96-98], nanocrystals (e.g., $Fe(IO_3)_3$, $KTiOPO_4$, $BiTiO_3$) [99-102], as well as core/shell CdTe/CdS quantum dots as small as 10 – 15 nm in diameter [103]. The intense SHG signals were used for nanoscale imaging and to track nanoparticles in cells, tissues, and organisms [104]. Pantazis *et al.* [102] and Hsieh *et al.* [101] characterized SHG signals from $BaTiO_3$ nanocrystals and developed bioconjugated nanocrystals as probes for cell and *in vivo* imaging without photobleaching or blinking. After an injection of $BaTiO_3$ nanocrystals (~30 nm) into the zebrafish embryo, bright SHG signals could be detected in either superficial tissue or deep within organs in the zebrafish during development. Unlike fluorescent dyes, the SHG nanoprobes exhibit a narrow emission profile, resulting in a high signal-to-noise ratio (SNR) in the tissues with little auto fluorescence background [102]. Based on the intense SHG signals from $BaTiO_3$ nanocrystals, a harmonic holographic microscope has been developed for 3D imaging of nanocrystals in cells without scanning [105].The schematic of the experimental setup used for SHG studies is shown in the Fig. 1.

4.2. Theory of third harmonic generation (THG)

In nonlinear optics one normally starts with the expansion of the polarization P as a function of the applied field E. The third term with the third order susceptibility $\chi^{(3)}$ can be written as:

$$P_i(-\omega_1) = \ldots + \varepsilon_0\chi^{(3)}_{i,j,k,l}(-\omega_1;\omega_2;\omega_3;\omega_4)\times E_j(\omega_2)E_k(\omega_3)E_l(\omega_4) + \ldots, \quad (19)$$

where a sum over all frequencies *x* has to be performed and the Einstein convention of summing over double indices has been used. For most all optical applications the intensity dependent index of refraction (IDRI) $n_{2,I}$ is the relevant parameter which can be written as

$$n_{2,I} \cong 3\chi^{(3)}_{1,1,1,1}(-\omega;\omega;\omega;-\omega)/\left(n_0^2\varepsilon_0 c\right). \quad (20)$$

With n_0 the linear index of refraction and c the speed of light. The nonlinear susceptibility for THG $\chi^{(3)}_{1,1,1,1}$ (-ω;ω;ω;-ω) is a good estimate for the parameter for IDRI. The THG can be described by solving the Maxwell's equation and inserting a nonlinear source term in the resulting wave equation. Similar to SHG also in the case of THG phase matching between all generated harmonic waves can influence greatly the harmonic intensity due to the dispersion of the NLO material. The phase match and thus the total harmonic intensity can be varied by changing the propagation length *L* inside the material. When we focus only upon the most important parameters, the harmonic intensity $I_{3\omega}$ for a material is given by

$$I_{3\omega}\alpha\left|\chi^{(3)}_{1,1,1,1}(-\omega;\omega;\omega;-\omega)\right|^2 \times \sin^2\left(\frac{3\omega L}{c}\left|n_{3\omega}-n_{\omega}\right|\right)I_{\omega}^3, \quad (21)$$

where I_{ω} is the intensity of the fundamental wave and n_x and $n_{3\omega}$ are the index of the refraction of the fundamental and harmonic wave, respectively.In practice the thickness variation is simply accomplished by rotating a solid material (powder, sheet or thin film) or translating a dissolved material inside a wedge shaped cuvet. The nonlinear susceptibility measured by THG is completely originated by electronic effects, as the optical frequencies are far above the natural frequencies of all other contributions. It gives therefore in general a lower limit for the nonlinear coefficients as for many other NLO effects like the IDRI also the nuclei and even complete molecules can have a contribution. When a single photon, or two or three photons of the fundamental beam arein resonance with excited real states of the nonlinear material (Fig. 2), strong frequency dependent enhancement of the harmonic intensity is observed that can be absent in, e.g. the IDRI. In these cases THG seems to give an upper bound forthe nonlinear coefficient.

The resonances of $\chi^{(3)}_{1,1,1,1}$ (-ω;ω;ω;-ω) can be written as a complicated function of the energy and the transition matrix elements of the electronic states involved. In the case of three-photon resonance one

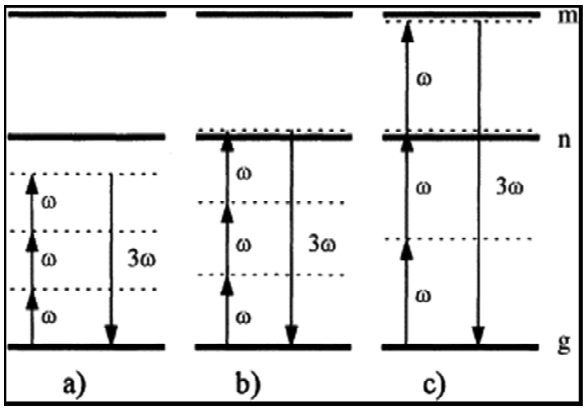

Fig. 2. Schematic representation of the THG process.

may simplify this expression by neglecting the imaginary part of $\chi^{(3)}_{1,1,1,1}$ (-ω;ω;ω;-ω) and other absorption terms. If one assumes that the main contribution to the three-photon resonance term also involves two-photon resonant terms one gets:

$$\chi^{(3)}_{1,1,1,1}(-3\omega;\omega;\omega;\omega) \; a1/\left[\left(E_{n,g}-3\omega\right)\left(E_{n,g}-\omega\right)\left(E_{n,g}-2\omega\right)\right]. \quad (22)$$

If one identifies the position of the first excitedstate with the wavelength λ_{max} of the linear absorption spectrum one is able to give an estimate of the enhancement due to this factor. In the wavelength region of 0:5 <λ/(3λ_{max}) < 0.9 the enhancement factor increases with a factor five. For a first assessment of the quality of NLO materials a value of the NLO coefficients within an order of magnitude is already sufficient. We therefore approximate the resonance function with a two-step function. This function will be considered to be a constant if *k* is outside resonance.If *k* is within 5% at resonance we set the enhancement factor to 10.

4.3. Third harmonic generation (THG)

The Third harmonic generation **(**THG) is a third-order NLO process that requires three photons (ω_1) in order to generate one photon at the tripled frequency ($3\omega_1$). Unlike SHG, THG is not restricted to noncentrosymmetric structures. The unique optical properties of nanostructures render them ideal THG enhancing agents. For example, the surface plasmon resonance from silver (e.g., 5 – 7 nm nanoparticle array [106], 30 nm nanoparticles [107]) and gold nanostructures (40 nm nanoparticles [108], gold nanorods with a length of 25 nm and aspect ratio of 3.727) enhances the THG process.

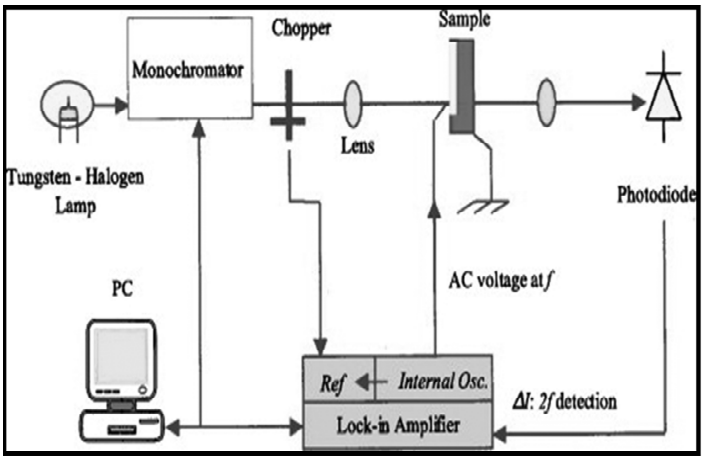

Fig. 3. Schematic diagram of the THG experimental setup.

Semiconducting nanomaterials also exhibit THG signals. Chang *et al.* demonstrated backward THG signals from ZnO thin films, CdSe quantum dots, and Fe_3O_4 nanoparticles [109]. Using a fs pulsed laser at 1290 nm, Jung *et al.* [110] discovered a strong THG signal from Si nanowires as small as 5 nmin diameter due to the large $\chi^{(3)}$ from crystalline Si, which is 1 – 2 orders of magnitude higher than materials such as crystalline CsS, TiO_2, and gold [111]. The intense THG signal has been used for label-free imaging of nanostructures in cells and tissues [112].The schematic of the experimental setup used for THG studies is shown in the Fig. 3.

5. NLO PROPERTIES OF NANOMATERIALS

The nanoparticles and nanostructured materials have attracted great interest in recent years because their properties such as quantum confinement of electrons and holes, surface effects, and geometrical confinement of phonons, are markedly different from those of bulk materials [113]. Nanoparticle has a rather large number of atoms, but itssize is comparable with characteristic dimensions describing the behavior of electrons and holes, thus creating an intermediate regime between molecules and bulk crystals [113]. A great deal of the recent interest in the optical responses of metal nanoparticles,nanoapertures in metal films, and metamaterials are focuses on enhancing local electromagnetic fields to enormous facilitate light–matter interactions [114]. The Enormous enhancement factors of 10^3-10^6 compared to the fundamental electric field at a flat metal surface has been predicted [114] and these strong local fields are particularly important for nonlinear optical processes, such as SHG and THG.

6. NLO PROPERTIES OF A SINGLE NANOPARTICLE

The optical nonlinearities of semiconductor nanoparticles are of great interest recently. So far their third-order nonlinear optical (NLO) properties have been widely studied. However, there are only few studies on second-order NLO properties, because it is believed that the centrosymmetry or near-centrosymmetry of spherical nanoparticles eliminates their first-order hyperpolarizability β values to zero or near zero. And for a long time it remains a problem to directly study the second-order NLO properties of such nanoscale particles by conventional NLO technique such as interfacial second harmonic generation (SHG) and electric-field-induced SHG techniques which are constrained by the orientational, size, and or charge restrictions [115]. Fortunately, the newly developed hyper-Rayleigh scattering (HRS) technique overcomes the above restrictions; hence second-order NLO properties of nanoparticles can be studied. Recently, a few studies were reported about HRS for the colloidal gold and insulator nanoparticle SiO_2 [116]. The HRS technique is used to measure second-order NLO response of a series of semiconductor nanoparticles with different surfaces prepared by different methods.

7. NONLINEAR OPTICAL PROPERTIES OF NANOCOMPOSITES

The polymer nanocomposites, consisting of semiconducting colloidal nanocrystals (NCs) embedded in polymer matrices, are original materials able to join the structural flexibility and convenient processing of the polymers with high carrier mobility,

bandgap tunability, and thermal and mechanical stability of the inorganic components. Such novel materials have been explored in many application fields, including linear and nonlinear optical devices, light-emitting diodes, optical switches, waveguides, sensors, and hard transparent coatings as protective layers [117 –122]. One of the most crucial points for the fabrication of such a class of nanocomposites relies on the ability to control the dispersion of the nanoparticles in the host matrix. In fact, nanoscale particles typically possess a strong tendency to aggregate, which might be detrimental for retaining their size- dependent properties. In nanocomposites, nanofillers must be finely dispersed in polymers so that the heterogeneous nature of the material should be evident only for sampling on a nanometric scale.

8. NLO PROPERTIES OF QUANTUM DOTS

Semiconductor nanostructures are considered as promising materials for multicolor single excitation biological labelling and dynamic three-dimensional nanoscale optical imaging. Large nonlinear optical coefficients in these materials may lead to photonics applications, such as ultrafast optoelectronic switches [122-128]. Moreover, nonlinear optical processes may provide valuable information for proper understanding of quantum confinement and surface effects in low-dimensional structures. The NLO properties of semiconductor nanocrystals have been investigated [122-135]. Recently beam distortion method, which is popularly called as the *z*-scan technique, has been widely employed to characterize the NLO properties of semiconductors. In the method of the *z*-scan, the transmittance of a nonlinear medium is measured as a function of the sample position in the *z*-direction. The transmittance function not only gives immediate information about the sign of the nonlinearity, but it also allows one to easily estimate the magnitude of the nonlinearity. The technique enables one to determine both the sign and the magnitude of the nonlinear refraction (NLR) coefficient of a NLO material.

9. NLO APPLICATION IN BIOLOGICAL

Metal nanoparticles have attracted great scientific and technological interest in biomolecular detection and clinical diagnostic application due to their specific physical and chemical characteristics. Several recently reported experimental results illustrated that nanomaterial based NLO assay can be used for monitoring chemical processes, biological and chemical toxins with excellent sensitivity and selectivity [50-74]. The Dendrimers are monodisperse hyper-branched molecules comprised of dendrons (tree-shaped units) attached to a central core; their well-defined and controllable structures have made them of great interest for a vast array of applications including drug transportation, light harvesting and optics [136]. Dendrimers containing metal centers have been synthesized for applications in (among others) catalysis, luminescence, sensing, and magnetic resonance imaging (MRI). Dendritic materials with enhanced nonlinear optical (NLO) properties have also attracted significant recent attention, because of the interest in modifying the propagation characteristics of intense light beams, of crucial importance to the emerging photonics industries. While the focus of most studies in the NLO properties of dendrimers has been with purely organic dendrimers [137], metal-containing dendrimers for nonlinear optics is a field of increasing interest.

10. CONCLUSION

In conclusion, in this review, an overview of the emergence of second and third order NLO nanomaterials for the development of nanomaterial based optical technology. Second order NLO materials are used in optical switching (modulation), frequency conversion (SHG, wave mixing), and electro-optic applications, especially in EO modulators. All of these applications rely on the manifestation of the molecular hyperpolarizability of the materials. It is requirement for nanomaterials for applications in second and third order harmonic generation. Thispaper also summarizes recent progress on the development of nanomaterials based NLO assay for chemical processes and sensing biomolecules and toxic metals.

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