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A review: Concept of Localized Surface Plasmon Enhanced Second- Harmonic Generation in Semiconductor- Metal Hybrid Nanostructures

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Abstract

Semiconductor-metal hybrid nanostructures and potential applications ranging optical sensing , photocatalysis and optical devices have brought interest due to a singular localized surface plasmon (LSP) effect for optical enhancement .LSPs in metal surface, excited by the interaction between light and electron plasma waves, arecapable of introducing an enhanced local electromagnetic-field, which has a great enhancement on a variety of optical processes spatially enhanced optical second-harmonic generation. This review article introduces acomprehensive seeing of physical mechanisms of optical second harmonic generation (SHG) in semiconductor metal hybrid nanostructures, and the enhancement of SHG by means of localized surface plasmon. This article includes the basic concept of; optical properties of semiconductor nanomaterials, Localized Surface Plasmon (LSP) , Hybrid Nanomaterials (HNs) (which include optical properties of hybrid nanostructures, motivation of hybrid nanostructures and the synthesis method of hybrid nanostructures), nonlinear optics properties which include , nonlinear optics properties of materials, second –harmonic generation SHG in semiconductor materials and the principles of enhance second – harmonic generation SHG effect.

1. Introduction

Plasmonic nanostructures are subwavelength sized metallic structures which interact with electromagnetic waves[1], e.g., light, on the basis of frequency selective, collective oscillations of the conduction electrons, the so-called plasmonic resonances. These resonances can be tailored by engineering the size and shape of the metallic structures and lead to a strong local intensity enhancement close to the metal structures for an incident electromagnetic wave. Due to their tunable optical response, plasmonic nanostructures are frequently used as the building blocks of metamaterials, which are man-made effective materials supporting unprecedented optical properties [1]. One class of optical processes, which can be strongly enhanced by both, optical resonances in matter and local intensity enhancements, are nonlinear optical frequency conversion processes. The most prominent and also first demonstrated among those is second harmonic generation, the instantaneous conversionof a strong electromagnetic wave into a new wave with twice the frequency inside a material lacking inversion symmetry. Several schemes to enhance SHG in nanostructures have been previous reported [2-5]. Hybrid nanostructures included of semiconductor and metal nanostructures has importance to improve the nonlinear

optical properties of semiconductors [6-8].

Plasmonics, which involves the coupling between electromagnetic radiation and collective electronic oscillations (or surface plasmons) in metals, is also relevant. The mechanisms of enhance nonlinear optical properties of plasmonic hybrid nanostructures are included surface-plasmon energy of the metal should match the emission photon energy of the semiconductor [9]. This mean the oscillation between the charge density of conduction electrons and its corresponding electromagnetic field would lead to a surface-plasmon resonance ,which provides an effective energy transfer channel between the metal surface and the emission semiconductor or vice versa. Secondly condition to achieve enhanced emission is: the distance between the semiconductor and the metal surface should be long enough to effectively suppress the significantly energy loss induced by the inevitable nonradiative energy transfer from the semiconductor to the metal [9]. There are many studies reported on the SHG enhancement of semiconductor-metal hybrid nanostructures which include (1) the demonstration of the SHG enhancement of semiconductor-metal hybrid nanostructures benefit the whole mode volume for an even-order nonlinear optical process, (2) the detection of a second order optical response from semiconductor-metal hybrid nanostructures. (3) High efficiency SHG response generated semiconductor-metal hybrid nanostructures. (4) Enhanced nonlinear response of single semiconductor nanowires by coupling to optical nanoantennas, and (5) enhanced optical signal in the near-infrared spectral range by using semiconductor-metal hybrid nanostructures [3].

2. Optical Properties of Semiconductor Nanomaterials

The optical properties of semiconductor nano material result from the interaction of light with the compositionand atomic structure of the material. Color, luster, and fluorescence are examples of well- known optical properties [10]. Semiconductor nano-materials generally have direct transition band structure, wider range of band gap and larger ionic bond component. Meanwhile, the reduction of particle leads to the existence of obvious dielectric confinement effect and quantum size effect, which makes it one of the most promising research fields. Besides, with the rise of the ultra-short and ultra-intense femtosecond pulse laser, people begin to study various excellent properties of semiconductor nano-materials related of intense light. Gold nanoparticles and zinc sulfide are interesting examples; these substances exhibit different properties as bulk samples compared to nano sized samples. Bulk gold is yellow in color while nano-sized sample is red in color. Bulk Zinc sulfide(ZnS) is white in color, while nano-sized particle of ZnS is

transparent. The underlying principle governing the color changes between a bulk sample and a nano –sample can be explained as follows: when light is shone on pieces of metal, the photons strike the electrons in the metal. In bulk metal, electrons are free to move more or less randomly throughout the crystal structure of the metal. However in a very thin film of metal lying upon an insulator (such as glass), the electrons are confined to a thin region. When the light strikes on these electrons the electrons will move in a coherent wave, rather than being free to move randomly. These coherent waves of electrons are called surface plasmons. The size of these waves of electrons depends upon the thickness of the film. If an incoming photon has just the right wavelength, its energy will be completely absorbed by the metal, and tuned into a surface Plasmon. This is called surface Plasmon resonance, i.e. the incoming photon resonates with the kind of electron waves produced in the film. Photons that do not resonate with the metal film will be reflected back. Consequently when white light strikes upon such a metal the film selectively absorbs photons at a certain small range of wavelengths [10]. Another factor is larger surface area/ volume ratio. Since the nanoparticles have dominating surface, the Surface Plasmon (SP) effect takes place [11].

2.1 Strong absorption of broadband and blue shift of absorption edge

(1) Strong absorption of broadband, The wide bond vibration mode distribution in semiconductor nanomaterials makes the infrared absorption frequency range become larger, resulting in the broadening of infrared absorption band. Meanwhile, the reduction of the size of nano-materials may lead to the reduction of the reflection of visible light by nano-materials, and thus increase the light absorption. Therefore, the strong absorption phenomenon of broadband may appear in the nano-materials [12]. (2) Blue shift of absorption edge, Blue shift may occur in the light absorption of bulk material and semiconductor nano-structure. This phenomenon is mainly caused by the following two aspects: First, the quantum confinement effect [12]: the reduction of crystal size can cause the broadening of optical band gap and finally result in the blue shift of the optical absorption edge; Second, the surface effect: The reduction of the crystal size of the nano-materials will cause the increase of surface tension. Besides, the crystal lattice will become distorted and lattice constant will become smaller.

2.3 Nonlinear absorption and radiation

(1) Saturated absorption. The absorption light decreases with increasing light intensity. When laser acts on the nonlinear medium, the phenomenon that the absorption coefficient of the medium decreases continuously and gets saturated with the increase of incident light intensity is called the saturated absorption (SA). This means the absorption cross-section is larger than the excited absorption cross-section of the medium in ground state. In the laser mode-locking and Q modulation, the medium can reduce loss and improve the laser output characteristics, which have important application value. (2) Reverse saturated absorption, when laser acts on the nonlinear medium, the phenomenon that the absorption coefficient of the medium increases continuously with the increase of incident light intensity is called the reverse saturated absorption (RSA). This means the excited absorption cross-section of the medium in ground state is larger than the absorption cross-section. The optical limiting feature that RSA can absorb the

strong light through weak light can be applied to the laser protective eyewear to protect the eyes of users by avoiding the damage of laser to the eyes.

(3) Two-photon absorption and two-photon fluorescence (TPA) & (TPF) effects

Two-photon absorption (TPA) refers to the phenomenon that when two photons of light at frequencies($\omega 1$ and $\omega 2$) are incident to the nonlinear medium, if the sum of the two frequencies is close to certain transition frequency in the medium, the two photons of light decay and are absorbed by the medium at the same time. The two-photon fluorescence (TPF) refers to the medium radiates a fluorescent photon while absorbing two photons. TPA and TPF effects can be applied to the high-resolution imaging devices and optical limiter [13, 14].

2.4 Photoluminescence and laser properties

When the medium is excited by light, the atoms or ions in the medium will jump to the excited state from the ground state after absorbing photons. But the excited atoms and ions are not stable and will return to the ground state while radiating energy and the photon with two energy level differences, which is called photoluminescence (PL). Simply, it is the luminescence occurring in the radiation recombination after the thermal equilibrium of electron hole pair generated when the light excites the sample. Generally, the luminescence of semiconductor nano-materials is spontaneous radiation, but when the energy of exciting light is high enough, the luminescence of the sample may be transformed from spontaneous radiation to stimulated radiation and even generate laser. Resonant cavity and optical gain medium are the two basic conditions to achieve laser. According to different resonant processes, the generating mechanisms of laser by semiconductornano-materials can be divided into random laser, whispering gallery mode (WGM) and Fabry-Perot (F-P).

2.5 Nanometer optical waveguide

For the one-dimensional semiconductor nanostructure, the axial dimension is large, but the radial dimension issmaller or nearly equal to the visible wavelength. Thus, the photon is under the confinement effect along theradial direction and can only transmit along the axial direction. Hence, the one-dimensional semiconductor nanostructure may produce optical waveguide effect and have the functions of optical waveguide devices. Thewaveguide generated by the semiconductor nano-structure is from spontaneous light, which is conducive tocoupling and can greatly reduce the optical loss. Besides, because the semiconductor structure has large refractive index, its refractivity with the air can help enhance the binding effect of the light beam.

2.6 Second harmonic generation (SHG)

The phenomenon that nonlinear optical effect is generated by direct frequency multiplication of exciting light is called the second harmonic generation (SHG).Compared with the UV radiation induced by two-photon or multiphoton, SHG is more convenient and effective, which has good application prospect in microscope imaging[15], nonlinear optical frequency converter[16], all-optical signal processor[17] and other fields. As reported, SHG in several materials, such as ZnO[18], CdS[19], ZnTe[20], ZnS[21] and GaAs[22], have been investigated. However, SHG in nanostructures is still limited by the relative low conversion efficiency for practical applications of nanoscale coherent light sources and integrated optical circuits. Therefore, many previous works have focused on improving the SHG conversion efficiency in kinds of nanostructures. Especially, hybrid nanostructures consisted of semiconductor and metal nanostructures have attracted wide attention due to the unique localized surface plasmon (LSP) effect for optical enhancement [23]

3. Localized Surface Plasmon (LSP)

The interaction of light in a field with metal nanostructures is defined by means of their strong interaction between the free electrons of the metal nanostructures and the incident wavelength of the semiconductor nanostructures. Here the metal nanostructures do as a source to transfer light into localized electric field in metal [24]. And called as localized surface plasmon (LSP) .LSP is an optical phenomena generated by the interactionof incident light and the free electrons of metal nanoparticles (NPs) that are smaller than the incident wavelength and its depend on the size, compositions and geometry. [25]. There are many famous material used as metal nanoparticles foe example Ag and Au, which due to the energy levels of transitions exhibit LSP in the visible range of the spectrum the sharpest and strongest bands among all metals, for biological applications Au is more desired because the biocompatibility and the inert nature [26]. Spherical metal nanoparticles harbor a set of quantized oscillation modes called LSP. These modes do not propagate and unlike some plasmon modes, they can be excited by direct light incidence. They occur in metallic structures with very small (nm scale) dimensions when they couple to an electromagnetic field. On the other way, we can define LSP are non- propagating excitations of the conduction electrons of metal nanoparticles (MNPs) coupled to the EM field (Figure 1) [24,27-29]. These modes arise from the scattering of sub- wavelength conductive MNPs as a result of excitation of the conduction electrons which experience a vestoring force due to the surface curvature of the particles.

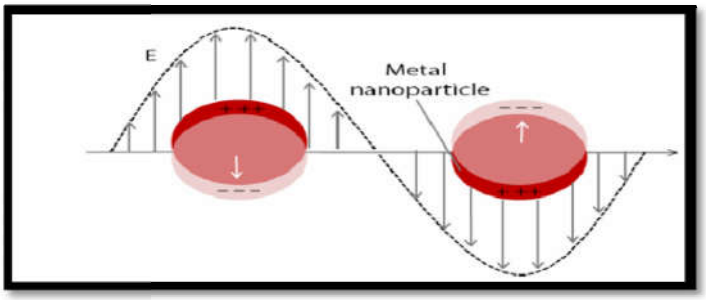

Figure 1. Schematic illustration of a non-propagating localized surface plasmon.

Michael Faraday reported in 1857 a systematic study on the synthesis of gold colloids and their respective colors [30]. This opened up the way and has maintained occupied scientists to this day developing a broad variety of synthetic protocols to produce nanoparticles with the desired shape, size and surface properties [31]. He showed that when the wavelength of light is larger than the radius of the metal nanoparticles, they exhibit a strong absorption band in the visible region. This phenomenon was attributed to a small particle effect, absent in bulk metals and individual atoms. Incoming electromagnetic radiation induces the formation of a dipole in the nanoparticle, a restoring force is then set up to compensate this, what results is a resonant plasma frequency matching the electron oscillation within the nanoparticle. These oscillation modes are known as surface plasmons and are characterized by a strong field enhancement at the interface between metal and dielectric [32,33]. The optical properties of metal nanoparticles are strongly affected by their composition, size and shape, but are also sensitive to their aspect ratio,[34] the environment [35,36] and the distance to other metal particles [37]. For example bulk gold shows a yellow color in reflected light, but in transmission thin films look blue, becoming more reddish as the particle size is reduced to ca. 3 nm.[37] This phenomenon is the result of the interaction of the oscillating electric field of an electromagnetic wave with the metal nanoparticles, which induces a dipole over the metal surface and makes the conduction electrons oscillate to restore the equilibrium electron distribution. Thus, when resonance is achieved it is known as localized surface plasmon resonance (LSPR).[38]Gold, silver, copper and alkali metals show plasmons in the visible region of the spectrum, giving their intense characteristic colors. This optical phenomenon is not limited only to these metals, since recently has been reported the presence of plasmons in the NIR region on vacancy – doped semiconductor nanocrystals such as copper chalcogenide.[39-41] It is worth noting that when metal nanoparticles are sufficiently close to each other, a larger enhancement of the electromagnetic field is produced at the interparticle gaps when exposed to an external light, with applications in photonics, photocatalysis or surface enhanced Raman scattering . gold nanoparticles offer a variety of applications.

Multifunctionality is the keyword to denote gold nanoparticles. In the recent years, gold nanoparticles are also extensively researched for their applications in biology. In addition to the high electron density, which offers good contrast, facile synthesis, they also have good biocompatibility, thanks to the inertness of gold [42]. Their use as contrast agents in cellular and biological imaging is tremendous since they are found to be easily conjugated to the commonly used biomolecules [43-45].

4. Hybrid Nanomaterials (HNs)

4.1 Optical Properties of Hybrid Nanostructures

The optical properties of a material are due to the interaction between incident light and atomic structure of the material. Color, luster, and fluorescence are examples of well- known optical properties. At the nano-scale, some interesting optical properties emerge For instance gold nanoparticles and zinc sulfide; these substances exhibit different properties as bulk samples compared to nano sized samples. Bulk gold is yellow in color while nano-sized sample is red in color. Bulk Zinc sulfide (ZnS) is white in color, while nano-sized particle of ZnS is transparent [46]. The underlying principle governing the color changes between a bulk sample and a nano – sample can be explained as follows: when light is shone on pieces of metal, the photons strike the electrons in the metal [47]. In the case of semiconductor-metal materials, the electronic properties of each component change. The interaction between the metal surface and the semiconductor leads to Fermi level equilibration (figure 2). In bulk systems, such an interface is characterized by the space-charge region and the corresponding Schottky barrier [48]. In the semiconductor nanocrystal the electrons are confined and the individual nanocrystal remains is energetic. Due to such size limitation the bands remain flat and the charge separation is essentially dictated by the Fermi level equilibration [49].

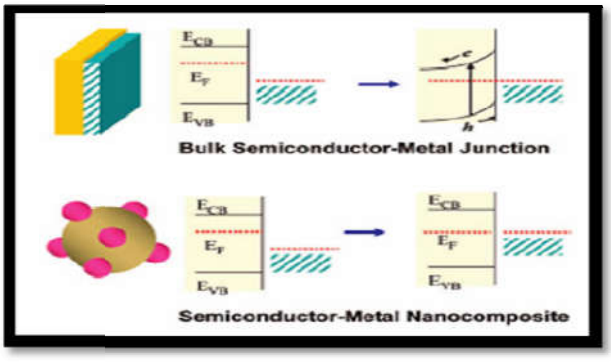

Figure 2: Electronic properties of hybrid materials - Bulk and nanoparticle junction (taken from [49])

As a result, the optical properties, such as the absorption and the photoluminescence of metal semiconductor nanoparticles are different from the sum of the spectra from each component [50, 51]. An interesting possibility for application is based on the charge separation in the hybrid nanoparticles. This process is of great importance in photovoltaics and photocatalysis [49]. Metal-semiconductor hybrid nanoparticles lead to a significant progress in nanoelectronics, because the metallic part serves as an electrical contact and as well enables self-organization [52].The physical and chemical properties of hybrid nanostructure are based on their shape, size, surface and material. Controlling these parameters opens the possibility to control the properties of material, which are of strong interest with respect to further application [52].

4.2 Motivation of Hybrid Nanostructures

Hybrid nanostructures are of high interest in academic research. The presence of different materials in one system opens up many possibilities to change properties from these of each single component or of their physical blend [48, 50, 53]. Due to such unique opportunity, hybrid nanomaterials find wide applications in physical,chemical, and biological research [49, 50]. Surface plasmon at the metal surface, excited by the interaction between light and electron plasma waves, are capable of introducing an enhanced local electromagneticfield, which has a great enhancement on a variety of optical processes [54-56]. Metal-semiconductor hybrid nanostructures are one important class of these multifunctional materials. A direct contact between a metal nanocrystals and a semiconductor nanoparticle facilitates charge separation after exciton generation in the semiconductor, which gives an opportunity to influence the optical properties and provide a simple platform for enhancing nonlinear optical responses, which have potential applications in nano-probing and nano-sensing. Several schemes to enhance SHG in nanostructures have been previous reported [2-5]. Specifically, a semiconductor-metal hybrid nanostructure has attention to enhance the nonlinear optical properties of semiconductors [6-8]. As well as it provides the photoluminescence enhancement [50], where, the photoluminescence intensity of semiconductor nanoparticles can be changed [50, 52], the latter could be interesting for applications in biological detection. Furthermore, self-assembly methods already well developed for metal nanocrystals can be applied to form superstructures of semiconductor-metal hybrid materials [52]. Thus, hybrid nanostructures possess characteristics making them suitable building blocks for the development of nanomaterial-based devices. The synthesis route of the growth of gold nanocrystals onto semiconductor nanowires was reported by Mokari et al. [52]. CdSe nanorods and tetrapods react with gold stock solution yielding CdSe/Au hybrid nanostructures.

4.3 Synthesis of Hybrid Nanostructures

Hybrid nano structures include two types of functionalities at the molecular scale, and are usually composed of an organic and an inorganic part. Many hybrid materials exist in nature, in which the inorganic part provides stability while the organic part acts as a link to soft tissues. In this way, the combination at the nanosize level of inorganic and organic or even bioactive components in a single material has made accessible an immense new area of materials science, which may have extraordinary implications in the development of multifunctional materials. The most common preparation methods of these materials are [57]: 1. Template- based is a synthesis method of the hybrid nanostructures materials. This category can be divided according to the nature of the template into hard-template and soft-template methods [57]. 2. Colloidal The colloidal preparation method dependent on the size of the aqueous colloidal solution nanoparticles . Generally speaking, a finely dispersed system is in a high free energy state. The colloidal material will therefore tend to aggregate due to attractive van der Waals forces, but this can be prevented by electrostatic stabilization mediated by surface adsorbed ions or by steric stabilization in the presence of bulky polymers or hydrophobic legends [57]. 3. Sol–gel . is a method that included to chemical reactions which transfer a homogenoussolution of particle precursors (a sol) to an infinite molecular weight threedimensional polymer (a gel) typicallythis involves a hydrolysis reaction followed by condensation polymerization, 4. Electrodeposition*"* is used the applied voltage to induce chemical reactions in an electrolyte solution. This method, including electroless deposition, is widely applied in the synthesis of one-dimensional nanostructured materials, typically with the aid of templates [58]. The instance of hybrid nanostructures are Au/ZnS [64], Ag/ZnS [65], Au/ZnO [66],Ag/ZnO [67], Au/ KNbO3 [68], and Al/ZnO nanostructures [69].

5. Second - harmonic generation (SHG) in Semiconductors Materials

Second harmonic generation (SHG) is a nonlinear optical process in which two photons of one wavelength (λ) are interacted to form a single photon at half the wavelength and at double frequency (2ω) [70]. Figure3 (a) shows the mechanism of SHG in semiconductor nanowires, hence a semiconductor nanowire optically excited at the fundamental frequency ω, it emits the optical frequency at the double frequency 2ω [71] exactly, (b) shows the energy diagram of the SHG. The solid line in the figure represents the atomic ground state, and the thin lines represent virtual levels.

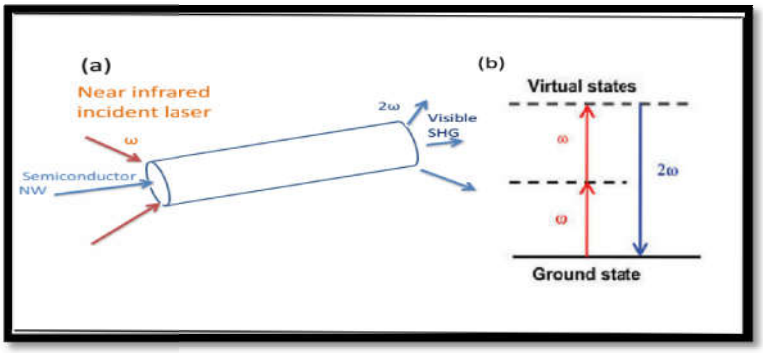

Figure 3. (a) Diagram of the SHG mechanism in semiconductor nanowire.
(b) Energy-level diagram describing second- harmonic generation.

Consider a monochromatic beam of amplitude E_0 and angular frequency ω, expressed as

$$E= E_0 \sin\omega t \quad (1)$$

When this electric field is incident on a nonlinear material, the resulting electric polarization is

$$P= \varepsilon_0 \chi E0 \sin \omega t+ \varepsilon_0 \chi^2 E0^2 \sin2 \omega t+ \varepsilon_0 \chi 3 E_0 3 \sin3 \omega t \ldots..(2)$$

Using basic trigonometry, the polarization can be rewritten as

$$P= \varepsilon_0 \chi E_0 \sin 2\omega t+ \varepsilon_0 \chi^2 E_0^2(1-\cos 2\omega t) + \varepsilon_0 \chi 3 E_0 3 (3 \sin \omega t – \sin \omega t)+\ldots(3)$$

The second harmonic term of the polarization is therefore:

$$P^{(2)}= \varepsilon_0 \chi^2 E_0^2(1-\cos 2\omega t) \quad (4)$$

Equation (4) shows two points of interest in the second harmonic term. The first term suggests that the secondorder polarization consists of a component at zero frequency, known as optical rectification [74]. This term does not lead to the generation of electromagnetic radiation. The second term corresponds to changes in the electric polarization at twice the fundamental frequency, generating light that radiates at frequency of. This process is commonly known as

second-harmonic generation, or SHG [75]. Effect of second harmonic generation refers to directly stimulate the optical frequency multiplier a non- linear optical effect. In 1961, the Fraken team [76] laser pulse Ruby laser (wavelength of 694.3nm) focused on the quartz wafer, successfully observed 347.2nm UV wavelength second harmonic generation. Compared the two-photon or multiphoton absorption induced by UV radiation, SHG is a more convenient and effective method, microscopic imaging of in [18, 77,78], nonlinear optical frequency converters [79] and all-optical signal processing [80, 81], and so there is a good prospect. At present, semiconductor materials, such as ZnS [83] ZnO [77], GaN [84], GaAs[85], CdS[86] and ZnTe[20] SHG in reports. Strong optical nonlinear effects in the field of physical mechanisms are as follows [86,87]: (1) electronic effects. Strong light field in the media, will bring about changes in the electronic distribution of atoms or molecules in the medium, thus causes the refractive index change. Electronic effect the response times for the 10-14 ~ 10-15 s. (2) the reorientation and redistribution. In bright light under the field, containing anisotropic molecular medium, HF Kerr effect refractive index change is mainly caused by reasons. Molecular reorientation response time is about 10-11 ~ 10-12 s. (3) the electrostrictive effect. When strong light field, electro magnetostrictive effect will bring about changes in the density of the medium, thus causes the refractive index changes, the response time is about 10-8~ 10-9 s. (4) heat. Media absorbs laser energy through a non-radiative transition into thermal energy, lead medium temperature, density changing, causing the refractive index changes. Thermal response time of approximately 1 ~10-8 s. In general, different nonlinear media, as well as different kinds of laser pulse width, the main mechanism is effects of different, and can sometimes be several mechanisms of interaction, which required under specific conditions for analysis. SHG has been observed from various types of nanomaterials, including metals [88–91], semiconductors [92–96], dielectric [97–100], and organic nanomaterials [101,102]. Since SHG only takes place in a non-centrosymmetric environment under electric dipole approximation [103], nanomaterials of noncentrosymmetric crystal structures are efficient in SHG such as ZnO[77 ZnS[83],BaTiO3[104] and KNbO3[68].The size of these nanomaterials ranges from 10–100 nm. As the SHG conversion efficiency of these nanomaterials is sufficiently high, these SHG nanomaterials have many potential applications such as imaging probe due to:
1- Tunable: SHG frequency is exactly twice of the frequency wave. Therefore, SHG frequency tuning can be done by tuning the incident frequency [105]. Moreover, SHG at nano-scale is a nonresonant process (without phase-matching requirement), providing a broad flexibility of choosing the best excitation wavelength or the emission SHG wavelength.
2- Coherent: The virtual-state transitions of SHG processes lead to the coherence between the signal and the excitation. As a result, SHG nanoprobes act as subwavelength coherent photon sources [105, 106, 107]. the complex field information of the SHG signal offers opportunities for new imaging techniques, such as scan-free 3D imaging [108, 109] and imaging through turbid

media by optical phase conjugation [106, 107].
3- Polarization sensitive: SHG signal from crystalline structure is generally dependent on the excitation polarization [103]. As a result, a polar measurement from the far field gives information about the crystalline orientation at nano-scale, offering a new degree of freedom for controlling and detecting the SHG signal [93,97, 100].
4- Stable: SHG does not involve any real-state transition, stable signal is ideal for dynamic and long-termimaging [100].

6. Principles of enhance second-harmonic generation effect

In general, nonlinear effects are very weak especially for high-order nonlinear processes due to the small magnitude of nonlinear susceptibilities. As a result, in order to excite efficient nonlinear processes, high pump powers and long propagation lengths are typically needed. For example in the most common used semiconductor-metal hybrid nanostructures to enhance second- harmonic generation. To get enhance of second harmonic generation we should considered some factors such as [70,73]:

• Nonlinear materials with large nonlinear susceptibilities are needed.
• Suitable distances between the semiconductor and the metal nanostructures.
• Phase matching conditions are required in parametric processes.
• Strong optical mode confinement and large overlap integrals between interacted modes are welcome.
• The design of nanostructures with noncentrosymmetric shapes has become essential because of the centrosymmetry rule.

The SHG response from chemically synthesized and lithographed nanoparticles with various geometries has been investigated (Fig. 4).

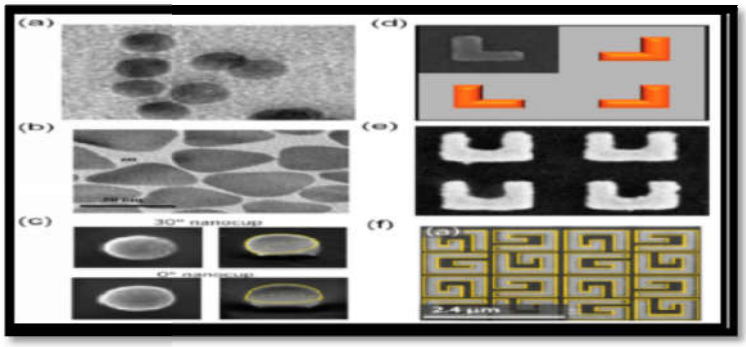

Figure4. Examples structures that SHG has been studied. Chemically synthesized nanoparticles adapted from reference [111]: (a) 20 nm gold nanoparticles, (b) silver nanoprisms], and (c) gold nanocups]. Lithographed nanoparticles: (d) L-shaped nanoparticles, (e) gold split-rings, and (f)

chiral G-shaped nanoparticles.

Often any shape can be designed, and such geometries contain, for example, gold nanostars [112], silver triangular nanoprisms [113], holes in metallic films [114,115], curved nanorods [116], split-ring resonators with U-shape [117-119], metal_dielectric nanodisks [120], gold T-dimers [121], nanocups [122], chiral G-shaped nanoparticles [123-128], chiral helix [129-131], L-shaped nanoparticles [132-136], or gold nanotips [137-139]. These different nanoparticle shapes aggravate specific properties of the nonlinear response and were thus designed for different aims. For example, L-shaped nanoparticles are basic plasmonic elements with noncentrosymmetric shapes and are efficient to increase the typically SHG intensity in the backward and forward directions. Split-ring resonators support magnetic modes maintain also high SHG intensities, besides being the elementary constitutive elements for a huge several of metamaterials. Chiral nanostructures have also been designed; the SHG response from these structures based on the fairness of the incident light leading to the socalled SH circular dichroism [140,141]. Superchiral metasurfaces combine the chirality of light with that of nanostructures and induce strong SH intensities [142]. Besides the study of nanostructures, that of nanoholes in metal nanofilms has also been made as mutual systems in the sense of Babinet principle for nanostructures. The possibility to observe extraordinary light transmission, where the transmitted intensity is much higher than the one expected from the geometric aperture area, has driven this research [143]. In comparison with nanoparticles, nanoholes and nanocavities can support higher incident peak intensities due to the fast heat dissipation in the metallic film, resulting in a higher damage threshold. It is interesting to note that a noncentrosymmetric shape does not necessarily result in a stronger SHG intensity, and further symmetry issues can arise despite the lack of centrosymmetry. For example, the nonlinear efficiency of noncentrosymmetric decahedra with five fold symmetry is identical to that of centrosymmetric spheres with identical sizes due to the cancellation of the nonlinear emissions from their different facets [144]. A symmetry relation often encountered in this framework, and particularly in the case of nanoparticle arrays, is the mirror symmetry. If a mirror symmetry is actually present, then the SH wave propagating along the forward and backward directions is polarized in the symmetry plane due to the spatial reversal of the nonlinear polarization and cancels in the other direction [145]. A dramatic consequence arises when the nanoparticle array exhibits two orthogonal mirror planes: the SH intensity vanishes in these directions, although the constituting nanoparticles are not centrosymmetric [146]. This particularity must be kept in mind for the design of nanostructure arrays. It may also result in surprising observations for coupled nanostructures (Fig. 5). One could naively think that the high fundamental field observed in narrow gaps [147] induces a strong SHG. Actually, this is not the case, and the reverse, the silencing of the SHG from plasmonic nanoantennas, has been pointed out [148]. Although the strong field enhancement

observed in the gaps at the fundamental wavelength results indeed in a strong nonlinear polarization [149] the nonlinear polarization vectors standing at each sides of the nanogap are out of phase and their contributions to the SH wave tend to cancel out in the far-field region[150,151]. This silencing of the SHG response is partially suppressed in nanogaps with noncentrosymmetric geometries, as those observed in gold nanoparticle dimers with T-shapes [152] or structures composed of two arms with different sizes [153, 154]. This silencing is a direct consequence of the symmetry properties of SHG and, as such, is not detected for third-order nonlinear optical processes such as THG and FWM. These examples further emphasize one more time the unique properties of SHG. Here, a clear separationhas been made between the centrosymmetry breaking induced by the nanoparticle shapes and the electromagnetic fields. The distinction is, however, not unambiguously defined since both effects are deeply interconnected. The case of spherical nanoparticles is a good example to illustrate this remark. For the smallest nanoparticles, the origin of the SH response is their nonperfectly symmetric shape (Fig. 5a), but as the nanoparticle size increases, the role played by the retardation effects becomes more important [155]. The transition from a dipolar SH emission induced by shape effects to a quadrupolar SH emission induced by retardation is a good example of the interconnection between the geometry of the nanostructure (size, shape, etc.) and the properties of the electromagnetic fields at both the fundamental and SH frequencies [155].

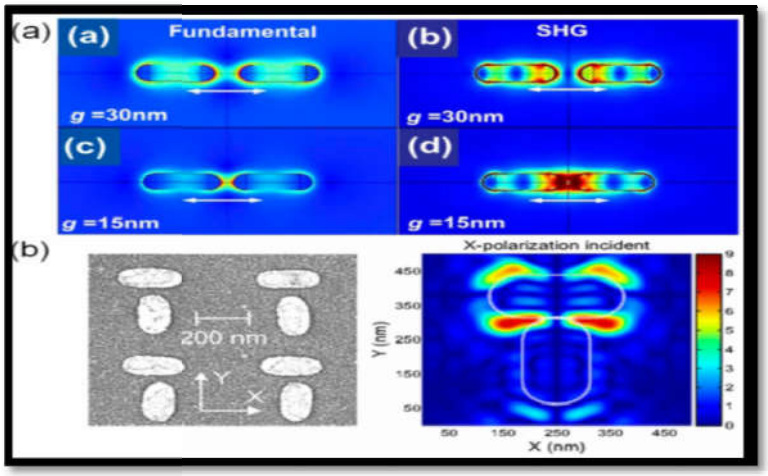

Figure 5. SHG from coupled nanoparticles: (a) gold nanoantennas and (b) gold T-dimers. Panel (a) (adopted from ref. 121). Panel (b) (adopted from ref. 153).

7. Conclusions and outline

In this article review conclusions we have focused on the concept of localized surface plasmon enhanced second-harmonic generation in semiconductor- metal hybrid nanostructures, and provides the reader with a very informative information about it, The outline of this review

article introduces a comprehensive seeing of physical mechanisms of optical second harmonic generation (SHG) in semiconductor metal hybrid nanostructures, and the enhancement of SHG by means of localized surface plasmon. This article includes the basic concept of; optical properties of semiconductor nanomaterials, Localized Surface Plasmon (LSP) , Hybrid Nanomaterials (HNs) (which include optical properties of hybrid nanostructures, motivation of hybrid nanostructures and the synthesis method of hybrid nanostructures), nonlinear optics properties which include , nonlinear optics properties of materials, second –harmonic generation SHG in semiconductor materials and the principles of enhance second – harmonic generation SHG effect.

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