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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.11, pp 4678-4681, Oct-Nov 2014

Second Harmonic Generation of Nanoparticles: An Overview

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Abstract: Second-harmonic generation (SHG) nanoparticles show promise as imaging probes due to their coherent and stable signals with a broad flexibility in the choice of excitation wavelength. In this paper, the polarization-dependent SHG responses of individual nanoparticles are studied in detail. From the measured polar response of a nanoparticle, we are able to find the orientation of the nanoparticle. We also examine the SHG response of the nanoparticles under different excitation polarizations, including linearly and circularly polarized excitations. We observe no toxicity of the functionalized nanoparticles to biological cells. To achieve specific labeling of proteins of interest, we couple antibodies covalently onto the nanoparticles. Specific labeling of cell membrane proteins with SHG nanoparticles for SHG live cell imaging is achieved. The coherent SHG signal radiated from the nanoparticles offers opportunities for new imaging techniques.
Key words: Nanoparticles, SHG, Imaging probes, Polarization.

1. Introduction

In the days, light was a significant tool in studying science. Through light-matter interactions, such as scattering, reflection, refraction, absorption, and photoemission, the propagating light field carries the information of the object under study, which allows us to observe it at a distance. Light introduces minimal perturbation during the observation and it readily propagates in free space. Therefore, light is extremely useful and convenient for sensitive detections. Technological advances in light sources, optical filters, computer hardware, and photon-counting detectors have been extensively employed in optical imaging systems. Extremely sensitive imaging systems have been demonstrated [1], which allows us to quantitatively analyze the chemical reactions on the single-molecule level [2]. Every imaging system needs a contrast mechanism. One of the most efficient methods of creating a contrast in an imaging system is to change the color of the signal away from the color of illumination. By using optical filters, one can efficiently reject the illuminating wavelength and allow only signal wavelength to arrive at the detector. Photoluminescence is the most widely used mechanism for wavelength conversion in imaging. In particular, fluorescent imaging probes are especially popular in the study of biology due to their satisfactory brightness, biocompatibility, and small physical size [3]. Fluorescent proteins can be encoded into genes and introduced into living cells, and the cells will produce these fluorescent proteins when expressing the gene, which is convenient in biological studies [4-5]. Besides fluorescent proteins, organic dyes [6] and quantum dots [7] are also popular fluorescent probes. The challenges of imaging with photoluminescent signal can be solved by nonlinear optical (NLO) processes which are also known for wavelength conversion. In NLO processes, the light-induced polarization of the material responds nonlinearly to the electric field of the excitation light, leading to radiations at harmonic optical frequencies [8]. Since the NLO processes do not involve any real-state transition, so the problems of photo bleaching and blinking are circumvented [8]. Among all the NLO processes, second-order nonlinearity, such as second-

harmonic generation (SHG), is particularly interesting because it is only efficient in non-centrosymmetric environments [8]. Therefore, SHG provide high contrast in unstructured and isotropic environments. The aim of this short review is to describe the highlight Second-harmonic generation (SHG) nanoparticles for potential applications.

2. Second-harmonic generation imaging (SHGI)

SHG microscopy has been developed as a standard nonlinear microscopy since the 1970s [9, 10]. The excitation wavelength is usually in NIR and the SHG signal is at exactly half the excitation wavelength, which is in the visible spectrum. Such a SHG scanning microscope is compatible with two-photon fluorescence scanning microscopy [11]. The quadratic dependency of the signal to the excitation power provides the optical sectioning capability in the axial direction, which is appealing to three-dimensional (3D) scanning imaging [12, 13]. The multi-photon microscopy is also ideal for deep tissue imaging because the scattering of the sample is less severe at longer excitation wavelengths [14]. SHG scanning microscopy has been used for examining endogenous structures in label-free biological samples [15]. Ordered and highly polarizable biological structures, such as collagen [16], muscle [17], and microtubules [14] are efficient in SHG, and therefore they show high contrast in a mostly isotropic environment in SHG images. In biological samples, the molecular structures and orientations determine the nonlinear susceptibility. As a result, the polarization-dependent measurement of the SHG signal can be used to study the molecular structures of biological samples [18]. While the endogenous SHG signal is attractive for label-free non-invasive imaging, exogenous SHG markers are also desirable due to the flexibility of having the SHG contrast from any target of interest. The development of SHG contrast agents began from organic dipolar molecular systems where the optical nonlinearity arises from the intramolecular charge transfer [19-21], referring to the SHG dyes. These SHG dyes have been demonstrated effectively for biological membrane SHG imaging. The asymmetric styryl dyes label only the outer leaflet of the lipid bilayer of the biological membrane, which satisfies the non-inversion symmetry requirement for an efficient SHG process [22]. Interestingly the SHG signal intensity of the dye molecule is sensitive to the local electric potential [23] and it has been shown as a novel approach for high-resolution detection for dynamic electrical activity of neurons [24].

3. SHG scattering from nanoparticles

The effective phenomena of SHG from nanoparticles can be seen as hyper-Rayleigh scattering (HRS). HRS was first studied with molecules where the nonlinear optical signal comes from the optical hyperpolarizability of the molecules [25]. SHG from nanoparticles is therefore very different from SHG in bulk materials where the SHG is usually governed by phase matching condition [8]. The SHG scattering from nanoparticles can be studied from calculating the linear scattering of the excitation field at fundamental frequency within and around the nanoparticles. The excitation field then induces microscopic SHG sources (dipoles and multipoles) at the locations where the second-order susceptibility is non-zero. For nanoparticles of centrosymmetric material, the bulk contribution disappears and other SHG sources are responsible for the nonlinearity. Surfaces are known for SHG by producing locally excited SHG dipole moments because the inversion symmetry is broken at the interfaces. Due to this surface specific SHG response, SHG has been exploited to the study of interfaces properties between two centrosymmetric materials [26]. Interestingly, this surface contribution vanishes when the shape of the nanoparticle is centrosymmetric, such as a perfect sphere. This is because the SHG sources at different parts of the surface of a sphere interfere with each other, and the overall SHG radiation vanishes due to the symmetry of the problem. It is worth noting that any deviation in shape from centrosymmetry leads to a nonvanishing SHG response [27].

4. Second-harmonic imaging of ZnO nanoparticles

The nonlinear optical properties of ZnO nanostructures are also attracting interest. Recently second- and third-order nonlinear coefficients of ZnO nanostructures were characterized [28], and SHG was observed from thin ZnO films and nanorods. Here we report bright SHG from isolated, ~300 nm agglomerates of ~20 nm ZnO nanocrystals. This is potentially important for biomedical imaging because ZnO is non-toxic, and thus could be incorporated into living cells. SHG images were obtained with acquisition time short enough for bio-labeling. From ZnO bulk which is noncentrosymmetric and has a large nonlinear susceptibility, so single-beam and two-beam configurations give rise of the same order of signal. When the size of ZnO nanoparticles goes down to a few nanometers, composites of randomly orientated nanopartilces are macroscopically centrosymmetric, so single-beam SHG from them is too weak to be detected. However, two-beam geometry can still give strong SHG as we recently reported that two orthogonally polarized beams can dramatically enhance

SHG from macroscopically centrosymmetric materials, e.g. SHG from Si nanocrystal composites was enhanced by a factor of 10^3 [29]. Smaller ZnO nanoparticles (e.g. size less than 20nm) which are better for bio-labeling are going to be prepared and imaged with two-beam SHG.

5. Second harmonic generation Analysis (SHGA)

The second harmonic generation measurements of the adsorption isotherm of malachite green to the surface of colloidal gold nanoparticles are performed with an experimental setup that has been described previously [30], with a few important modifications. Titanium: sapphire oscillator is pumped by a 4.5W 532 nm Nd: YVO4 laser producing 80 fs pulses centered at 816 nm with a repetition rate of 82 MHz and an average power of 500 mW. A 6.4 cm focal length lens focuses the p-polarized laser pulses to the colloidal sample in a 1 cm quartz cuvette at room temperature. The SHG light is collected at 90° and is refocused to a detector through a filter to remove scattered fundamental 816 nm light. The detector consists of a monochromator in front of a photon-counting photomultiplier tube (PMT) connected to a computer. A computer-controlled burette adds a high concentration malachite green solution to the colloidal nanoparticle sample during automated stirring. Several spectral scans are acquired for each addition of malachite green to ensure that a stable equilibrium is reached, and the isotherm is acquired several times for statistical analysis. A powerful technique for investigating the chemical and physical properties of molecules at colloidal nanoparticle surfaces utilizes second harmonic generation [31] and sum frequency generation [32]. The key attribute of these second order spectroscopies is that they are interface selective for reasons of symmetry [33]. The application of SHG to the study of interfacial phenomena complements important work in which molecules of interest are covalently bound to the surface of metal nanoparticles [34]. This SHG research has since been extended to study the adsorption of molecules to a variety of types and sizes of colloidal polymer microparticles and nanoparticles [31], clay [36], TiO2 [37], and carbon black [38] nanoparticles, oil droplets in water [39], as well as phospholipid liposomes bilayer membranes [40]. Related work using SHG to measure the surface electrostatic potential [41] and the surface acidity pKa [42] of nanoparticles has also been achieved.

6. Conclusion

Second harmonic generation has been used for the first time to probe freely adsorbing molecules that are located at the interface of metallic nanoparticles with the liquid in which they are suspended. The isotherm of malachite green adsorption to the surface of colloidal gold nanoparticles in aqueous solution has been obtained from measurements of the SHG signal as a function of the adsorbate bulk concentration. The SHG signal was found to be polarization dependent due to the tensor nature of the second-order nonlinearity. We observed a good agreement between the theory and the experimental results. Through a polar measurement, we can determine the orientation of the nanoparticle in the far field. With the knowledge of the polarization dependent SHG signal, we studied the SHG response under linearly and circularly polarized excitation. We found that circularly polarized excitation is usually inferior in terms of reducing the polarization dependency of the SHG signal. Interestingly, we also found that one could greatly reduce the polar response by using a rotating linearly polarized excitation at a rotation frequency much lower than optical frequency but higher than the integration time of the detection. Meanwhile, tightly focusing the excitation helps reduce the polarization dependency due to the depolarization of a tightly focused beam. SHG nanoparticles have shown promise as long-term biological imaging probes due to their non-blinking and non-bleaching signal. These SHG nanoparticles can be readily imaged with a standard commercial two-photon confocal microscope. We used a near-infrared femtosecond laser for the excitation of the nanoparticles with excitation intensity tolerable for biological sample. By further exploiting the coherence of the SHG radiation of the nanoparticles, we demonstrate light concentration on the nanoparticles behind a scattering medium via digital phase conjugation. This technique has the potential to improve the efficiency of photo-therapy as the biological tissue is generally scattering. Digital phase conjugation is a fast and efficient method to undo the scattering. The phase conjugated field traces back the scattering trajectory and focuses on the nanoparticle

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