Visible second-harmonic light generated from a self-organized centrosymmetric lattice of nanospheres

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Abstract: We designed and fabricated a centrosymmetric material where one may be able to consider an efficient quadratic nonlinear interaction. We followed a solid phase-supported organic synthesis methodology to covalently bind a large number of highly nonlinear molecules to the surface of polystyrene nanospheres. Such chemically modified optically nonlinear latex spheres, when suspended in water, are seen to perfectly self-organize into a centrosymmetric lattice. Taking advantage of the nonlinear interaction located at the sphere-water interface and the photonic crystal properties of the fabricated material we were able to generate second-harmonic light visible to the naked eye.

OCIS codes: (190.0190) Nonlinear optics; (190.4400) Nonlinear optics, materials; (160.4330) Nonlinear optical materials

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1. Introduction

As is well known a symmetry of inversion leads to the cancellation of the dipolar contribution to the second order nonlinear susceptibility. This is the reason why centrosymmetric solids, liquids, or non-stretched biological tissue are not suitable materials to consider second-harmonic generation. At present, one may grow or fabricate different types of noncentrosymmetric materials and, many of the laser light sources available today rely at some point on such quadratic nonlinear processes. Applications from the quadratic nonlinear interaction span across a wide range of disciplines in science and technology that go from optical control of data bits to microscopy imaging. However, the need for periodically poled or highly ordered materials sets important limitations on the performance and applicability of optical second order nonlinear processes as generation of light at higher frequencies, parametric amplification of light, or optical parametric oscillation, among others.

As is well known such noncentrosymmetry could also be obtained at the interface that separates two centrosymmetric materials. Although such surface SH generation (SHG) is measurable with the use of high peak power lasers and very sensitive measuring devices such as photomultipliers or avalanche photon counting modules, the contribution coming from a few molecular layers at the interface is roughly speaking 10^{-12} times smaller than the contribution from the bulk of a crystal of the same material a few millimeters in length [1]. In 1995, one of us proposed to use the large number of interfaces available in the bulk of a periodically structured material such as a three-dimensional (3-D) photonic crystal to enhance the surface contribution to SHG [2]. 3-D photonic crystals were fabricated from commercial sulfate latex of monodisperse polystyrene nanospheres where a nonlinear molecule was physically adsorbed onto the sphere surface. Although promising results were obtained, the energy conversion efficiency was determined to be around 5×10^{-13} [3]. The physical adsorption of charged nonlinear molecules formed a positively charged layer covering the negatively charged sulfate functional groups of the polystyrene sphere surface, which prevented self-organization of such spheres in a lattice when one attempted to adsorb a larger number of nonlinear molecules. As a matter of fact, the pioneering studies by Hiltner and Krieger [4], and by Carlson and Asher [5], of the Bragg diffraction of light at wavelengths in the visible from monodisperse suspensions of polystyrene spheres, already indicated that the specificity of the surface charge group, as well as, ionic strength in the surrounding water play a determining role in the ordering of such spheres.

2. Nonlinear centrosymmetric crystal preparation

It should be possible to obtain a photonic crystal for efficient second-harmonic generation if one achieves the double goal of a sphere with an unscreened surface charge and with a large surface nonlinearity. We selected as a support material a modified carboxyl/sulfate latex, which is commonly used in some immunology tests, where a covalent coupling of a protein or other active molecules to the sphere surface is required [6]. Then, it is possible to chemically bind the nonlinear molecule to the highly reactive carboxyl group while leaving the sulfate groups, responsible for the stability of the colloids, unaltered. In general, such binding is performed between amino groups of the protein and the carboxyl groups of the sphere surface. In the present work, we followed a solid phase-supported organic synthesis methodology to covalently bind a large number of molecules with highly nonlinear optical properties to the surface carboxyl groups of modified sulfate latex spherical nanoparticles. To form such nonlinear surface layer we chose Crystal Violet (CV), a molecule that when adsorbed on a plane substrate and compared in the same conditions to other donor/acceptor organic molecules, was shown to exhibit one of the highest efficiencies in the conversion of infrared light at 1064 nm to green light at 532 nm. When we compared, for instance, the efficiency of a monolayer of a stilbazonium salt such as DAST [7], with the efficiency of a CV monolayer, we found that the SH signal measured was 3.8 times larger in the CV than in DAST. Both molecules were modified to have a hydroxyl group to be linked to the functional carboxyl groups of the sphere surface [8]. From here after, such modified Crystal Violet will be referred to as ethanol CV. After the ester bond between the carboxyl groups and the modified CV was carried out, we determined, by quantitative UV-visible analysis, that coverage of the carboxyl groups, and consequently the yield of the esterification processes ranged from 60 % to 75% depending on some specific parameters of the chemical reaction. Given the size of the CV molecule and the fact we used 147 nm in diameter spheres, one may conclude that the sphere is fully covered by the ethanol CV.

As schematically shown in Fig.1, such spheres densely covered by a nonlinear molecule retain, however, the necessary stability due to the uncovered sulphate groups. The remaining stray ions in solution may be removed by placing the solution in a cuvette with an ion exchange resin placed in the bottom. Stray ions that screen the surface negative charge from the sulphate groups diffuse towards the resin, and then the range of the coulombian interaction between spheres is increased forcing a self-organization of such spheres into an FCC lattice [6, 7]. We used a 200 μm thick cuvette and we observe the formation of a crystalline structure as thick as the cuvette. As is well known the crystalline ordering takes place with the (111) planes of the FCC lattice parallel to the faces of the cuvette. By illuminating the crystal with a focused beam at 400 nm, we observed the pattern of the six Kossel lines corresponding to six reciprocal lattice vectors adjacent to the reciprocal lattice vector perpendicular to the faces of the cuvette [9]. No changes were apparent in such pattern when we moved the cuvette in a plane perpendicular to the beam direction, an indication of the formation of a single crystal domain of very good quality.
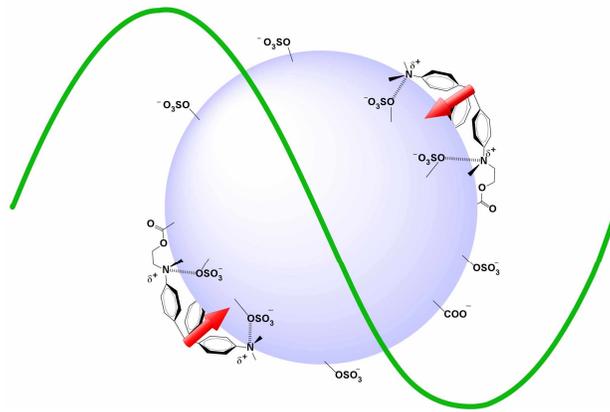
Fig. 1. Schematic representation of the ethanol CV bonded onto the polystyrene sphere surface. The pyramidal shape of the molecule results in a breaking of the centrosymmetry of CV as schematically shown with a red arrow. The green line corresponds to one wavelength of the SH light. While the sphere and the wave are drawn at a similar scale, the CV molecule is shown pictorially many times larger in relation to the other elements of the figure.

3. Quadratic nonlinear interaction in 3-D centrosymmetric photonic crystals

The 3-D photonic crystal obtained was pumped using 1 ps laser pulses at 1054 nm from an Nd: Glass laser and placed in a rotating mount with the rotating axis perpendicular to the laser beam. The laser pulses with an average energy per pulse of 1.4 mJ, were focused down to a spot of 1.5 mm in diameter. We performed a measurement of the generated SH light in transmission as a function of the angle of the normal to the crystal face with respect to the incident beam, shown in Fig.2. We observe, clearly, a narrow peak of SHG at the upper edge of the first order Bragg reflection band at 527 nm, which is centered at -36 deg., and a second peak corresponding to the symmetric band centered at 36 deg. At this edge the periodic structure induces a reduction in the effective index at 527 nm that is large enough to match the index at 1054 nm.
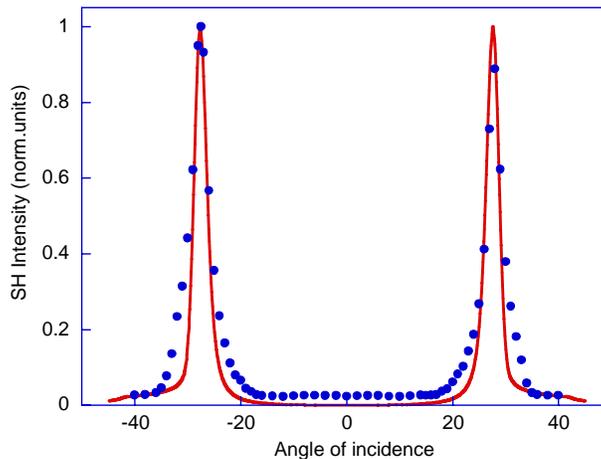

Fig. 2. Second-harmonic generation within a 3-D photonic crystal. SH intensity as a function of the angle of incidence. The blue solid dots correspond to the experimental measurements while the red solid line corresponds to a theoretical fit using the model briefly described in the text.

The frequency of the light at that last wavelength is very far from the first order Bragg reflection, and as a consequence its effective index remains unaltered. Nonetheless, such type of measurements cannot distinguish, in principle, between a nonlinear process of bulk origin from one of surface origin. We performed additional measurements of the s- and p-polarization SH generated light as a function of the polarization of the incident fundamental beam. These measurements when the incident angle corresponds to the angle of maximum generation at 28 deg. are shown in Fig. 3. Note that the polarization dependence observed is characteristic of a surface type generation [10], but to clearly understand the experimental measurements we consider a theoretical model that includes all 3-D aspects of the interaction taking place in such material structure: The ratio among the several nonzero elements of the nonlinear hyperpolarizability tensor, the spherical distribution of dielectric material in a unit cell, and the organization of the spheres in a 3-D lattice.
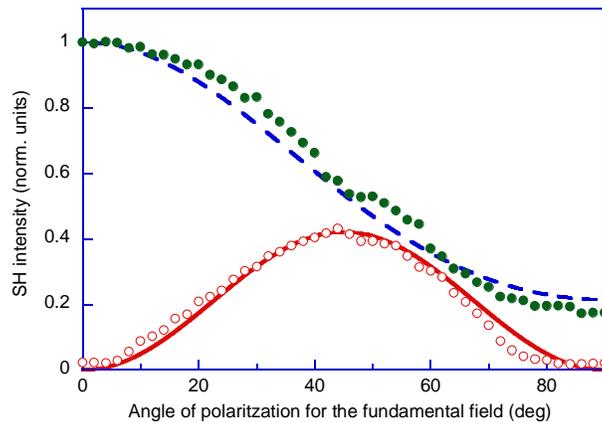

Fig. 3. Experimentally measured, p-pol (green solid dots) and s-pol, (red open circles) SH intensity as a function of the angle of polarization for the fundamental field. The blue dashed line and red solid line correspond to the theoretical fits using the same model mentioned above.

After the chemical bond between the nonlinear molecule and the sphere surface is formed the ethanol CV will lay flat on the surface of the charged polystyrene sphere. It has been reported that CV in a polar solvent or a charged environment for that matter will adopt a pyramidal structure with a C_3 symmetry where the central carbon would be at the top while the amino groups would be pulled towards the negatively charged surface of the sphere. This breaks the centrosymmetry of CV as shown schematically in Fig. 1 [11]. The sphere (CV + polystyrene), as a whole, constitutes an object that is centrosymmetric. There is, however, a local breaking of the symmetry at the surface. It has been shown theoretically that one can take advantage of that local breaking of the symmetry and get a nonvanishing, except in some high symmetry directions, scattered light at the SH frequency [12-15]. This becomes clear when one realizes that, as shown in Fig. 1, the diameter of the sphere is of the same order of half a wavelength of the light we are aiming to generate. The light at the entrance surface of the sphere has an electric field aligned with the dipole moment of the molecules on that surface, whereas at the exit the electric field has changed sign as the dipole did. To summarize, both contributions on either side of the sphere surface have the same sign, and consequently they add constructively. In our material, however, spheres are not isolated. On the contrary, they occupy the sites of an FCC lattice. A good approach to understand what the mechanisms are that lead to a positive contribution from the light generated by each portion of the sphere surface and then by all spheres together is by considering first the light generated simultaneously by all the spheres of one single plane of spheres and then add the contribution from all planes. In a given (111) plane of the lattice, the spheres are periodically distributed on

that plane forming a 2-D triangular lattice. This is very helpful since we may reduce the study of the contribution from the entire plane to the study of the contribution from one unit cell that contains one single sphere. Light incident at the fundamental frequency will induce a nonlinear polarization source that may be written, after contracting the nonlinear susceptibility tensor with the fundamental field, as:

$$P_i^{nl}(\mathbf{r}) = \chi_{ijk}^{(2)}(\mathbf{r})E_j(\mathbf{r})E_k(\mathbf{r}) \qquad \text{Eq. (1)}$$

Where P_i is one of the three components of the nonlinear polarization source, and E_j or E_k is one of the three components of the electric field amplitude. By symmetry considerations, one finds that only 5 of the 18 elements of the nonlinear susceptibility tensor $\chi_{ijk}^{(2)}$ are different from zero. Additionally, the $C_{v\infty}$ symmetry of a surface leads to only three different nonzero elements, which in spherical coordinates are χ_{rrr}, $\chi_{r\phi\phi}=\chi_{r\theta\theta}$, and $\chi_{\theta\theta r}=\chi_{\phi\phi r}$, where r indicates the radial direction, θ the polar angle, and ϕ the azimuthal angle. As in ref. [16] one may adapt the Green function approach for surface optics, first developed by J. Sipe [17], to consider propagation within a medium where the nonlinear material is localized at the surface of the spheres. We have extended the model in Ref. [16] to include contributions to SHG from all three of the non-vanishing elements. Applying such Green function integration approach we solve for the generated electromagnetic field at the SH frequency.

The solution we obtain retains the basic aspects of the nonlinear interaction from a single sphere that has been studied in the past, but adds some new features that are specific to the fact that spheres are ordered in a plane. For instance, the transmitted SH (from one single plane) would be zero. This is a result of the surface character of the interaction. In accordance, looking at Fig. 1 one realizes that the high symmetry of the dipoles distributed on the entire surface of the sphere would lead to a cancellation of SHG in the forward direction. This is not the case in other directions of a lesser symmetry with respect to the incident field. In the case when SH scattering from a single sphere is considered, one observes a quadrupole like pattern of generation [12, 14] however, in the case of a plane of spheres, the contribution from all spheres add constructively to generate SH light, shown in Fig.4, at an angle that obeys the law of reflection. That SH signal in reflection is dependent on the lattice parameter and on the diameter of the spheres. If the diameter of the spheres approaches zero, the local noncentrosymmetry is removed, and the nonlinear interaction in the dipole approximation would vanish. A very large diameter is not always desirable because there are several features that could reduce the effectiveness of the interaction, such as, for instance, cancellation from the surface contribution of adjacent spheres. We found that an optimum diameter is between 120 nm and 200 nm.

The final step towards an efficient generation is to be able to coherently add the contribution from all planes of the lattice. This is possible in photonic crystals where the periodicity alters the effective index of refraction of one of the interaction waves while the index for the other remains practically unchanged [18]. Such change in the effective index, results in a mechanism of phase matching that was first proposed for 1-D periodic structures [19], but has also been proven to be applicable to 3-D photonic crystals [2, 3]. This requires an ordering of the spheres into a photonic crystal, which, as mentioned above, is performed in our case in a 200 μm thick cuvette. To determine in what conditions, contributions from all planes add coherently, one may apply the transfer matrix to the solution obtained for one single plane. A numerical calculation predicts that when the first Bragg resonance of the crystal is in the neighbourhood of the SH frequency, the effective index at such frequency is modified to match the index to the fundamental wave. Since the SH wave propagates within a transmission resonance at the outer edge of the Bragg band, one would expect an additional enhancement due to a field localization, however, such an enhancement can only be seen when a very small number of planes is used, otherwise the dispersion in the size of the spheres partially destroys the coherent superposition of forward and backward propagating fields. Generation is nonvanishing in the reflection direction only, however, because of multiple

reflections, one obtains a SH peak in transmission as well. The SH intensity as a function of the angle of incidence for a crystal of 907 planes is shown in Fig. 4. The contribution from the entire set of planes is approximately 5330 times larger than the contribution from one single plane. Although phase matching is perfect, the increase in signal is not quadratically proportional to the number of planes because in the numerical calculation we included a 2% dispersion in the size of the spheres and an effective absorption coefficient to account for scattering losses and the linear absorption of the nonlinear dipole. The effective absorption coefficient used was obtained from a direct measurement of the transmission at 527 nm.
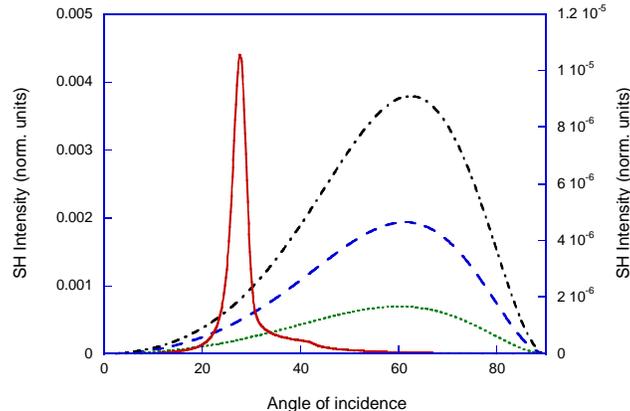
Fig. 4.   Second-harmonic generation from 1 plane and 907 planes. Reflected SH intensity from one plane (right-hand side axis) for spheres of 120 (green dotted line), 147 (blue dashed line), and 170 (black dot-dashed line) nm in diameter. Transmitted SH intensity from 907 planes (red solid line and left-hand side axis) of 147 nm in diameter spheres.

Using all the parameters of the actual nonlinear photonic crystal lattice in our numerical calculations, we may predict the reflected and transmitted light by the structure. If the same 2% dispersion on the diameter of the spheres is taken into account, one may accurately reproduce the experimental measurements of position and width of the phase matching peaks, as shown in Fig 2. Selecting the appropriate ratio between the three different nonzero elements of the nonlinear susceptibility tensor we accurately reproduce the polarization dependence of the measured SH as shown in Fig. 3. Note that our theoretical model does not include any contribution to SHG except the one coming from the nonlinear material located at the interfaces between the sphere and the surrounding medium. From such results we conclude that the sole contribution to SHG comes from the large number of inner interfaces of a centrosymmetric lattice, and that any other possible contribution, such as a quadrupole of the bulk of the material, is negligible.

4. Efficiency of second-harmonic generation

We performed a measurement of the efficiency of the process and we determined it to be 10^{-6} %. The conversion was measured more than 15 months later and no change in the efficiency was observed. Such conversion is more than one million times larger than the conversion one would expect from a bare photonic crystal of polystyrene spheres. The generated light is, in fact, clearly visible to the naked eye under dimmed lights. In Fig. 5, where a photograph of a small part of the experimental set-up is shown, we observe a spot of green light, which corresponds to the light diffused from a white card when the generated reflected beam was pointed towards that card. As it has been demonstrated recently, in a parametric counter-propagating interaction configuration, one could obtain, with very short materials of less than 100 μm, an amplitude conversion that would be approximately 30 times larger in the case where a modulation of the index of refraction is present, as opposed to the case where only a

modulation in the nonlinearity is present as in materials designed for quasi-phase matching [20]. Note that in that event, the efficiency from the new material we propose could be larger than the one from many bulk crystals with no structuring since the counter-propagating interaction would be perfectly phase matched in the former case. Any material that can hold such type of counter-propagating interaction is essential to lead to a backward parametric oscillation [21]. The backward parametric oscillators would have a broader tunable range, be more compact, more stable and eventually more efficient than existing ones [22].
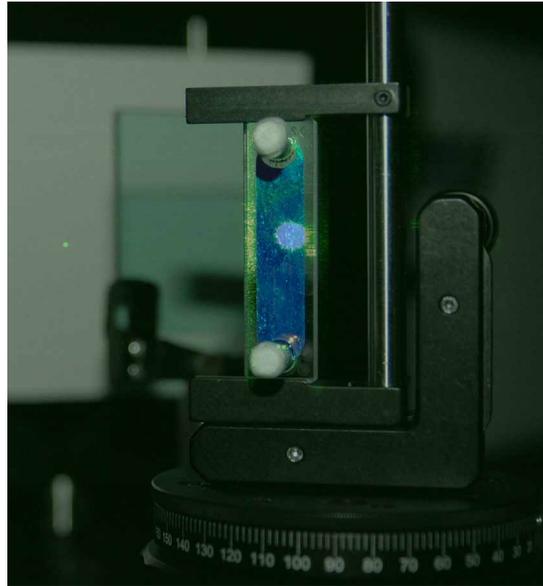
Fig. 5.   A picture of the generated green light diffused from a white card. The photograph was taken using a Nikon D70 digital camera with the room lights switched off and an exposition time of 25 seconds. This picture is superimposed with a photograph of a partial view of the experimental set up, taken using the camera built-in flash, where the CV colloidal crystal appears on the right hand side of the picture. From the photograph one sees that green light is generated in a very nicely collimated beam. The infrared laser pulse is coming form the right hand side of the picture and the generated light in reflection is coming form the opposite face of the crystal not visible in the picture.

5. Conclusion

To summarize, we provide a clear demonstration that centrosymmetric materials can also be made efficient. To reach a 10% efficiency in the energy conversion of light with a material similar to the one we propose, one would have to increase the number of nonlinear dipoles per unit volume, the nonlinearity of such dipoles and, the total length of the crystal only by a factor of 14, 7 on average, while reducing the effective absorption by the same factor. This opens the door for the development of a whole new class of more flexible nonlinear optical materials. In fact, the configuration we propose could be applied to many organic nonlinear molecules, which as single entities, exhibit large optical nonlinearities but a large number of them can not be organized in an appropriate configuration to meet the strict requirements of an efficient second order nonlinear interaction. Applications of such new materials go beyond the generation of light at higher frequencies. Almost 90% of the material surrounding the spheres is a centrosymmetric liquid. The surface nonlinear process we observe could be used as a powerful tool to study chemical species or biological components infiltrated in that medium. Moreover, in this material where no poling fields are needed the nonlinear molecules stay bound to the surface and remain with the same average orientation over a long period of time.

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