Tailoring second harmonic emission by ZnO nanostructures: Enhancement of directionality

Emilija Petronijevic* and Concita Sibilia

Sapienza University of Rome, SBAI Department, Rome 00161, Italy

Received 28 December 2023 / Accepted 28 February 2024

Abstract. Tailoring nonlinear optical properties at the nanoscale is a hot topic in nowadays nanophotonics, promising for applications spanning from sensing to ultrafast optical communications. Here we present a numerical approach of designing a simple semiconductor nanostructure able to tailor second harmonic emission in the near- and far-field. We start from linear simulations of ZnO nanospheres, which reveal multipolar nature of the scattering. Next, we show how the same nanospheres, with radii in 30–130 nm range, excited at 800 nm, manipulate the directivity of the emitted second harmonic. We observe that the nanospheres which exhibit Kerker condition at 400 nm, emit the second harmonic field in the forward direction. We further investigate how the asymmetry (ellipsoid geometry) tailors the second harmonic directivity. We finally introduce geometry with low chiro-optical response, and observe that the second harmonic far-field depends on the handedness of the light exciting the nanostructure at 800 nm.

Keywords: Nanostructures, Nanophotonics, Nonlinear, Electromagnetic simulations.

1 Introduction

Dielectric and semiconductor nanostructures in low refractive index media support both electric and magnetic resonances, thus controlling the scattered field directionality and intensity [1]. Their low ohmic losses in the near-infrared and visible light spectra offer advantages in novel nanophotonic components, aiming at applications in biosensing, emission control, and all-optical manipulation [2–4]. Furthermore, exploring nonlinear properties of all-dielectric nanostructured media offers unique possibilities to enhance harmonic generation and tailor its radiation pattern [4–7].

ZnO is a wide direct bandgap semiconductor already widely applied in industry. With the progress of nanotechnology, micro- and nanostructuring of ZnO showed promise in efficient room-temperature nanophotonic devices based on microcavities [8] and nanowires [9]. Moreover, ZnO is non-centrosymmetric, offering efficient nonlinear optical properties at visible frequencies [10, 11]. Combining well-developed colloidal manufacturing of ZnO [12] with electromagnetic tailoring of its nonlinear properties could open fertile field in colloidal nonlinear nanophotonics.

In this numerical work, we investigate linear and nonlinear optical properties of various single ZnO nanostructures, immersed in water. We perform simulations of multipole decomposition and investigate how the supported modes tailor the second harmonic response. Starting from the nanosphere geometry, we further introduce the asymmetry, and, finally, low chiro-optical response, showing that the far-field second harmonic distribution strongly depends on the nanoparticle shape and the incident polarization.

2 Results and discussion

We perform full-wave 3D simulations based on the finite-difference-time-domain (FDTD) method in Lumerical [13]. First, a single nanosphere of radius $r$ is considered for linear scattering in water (FDTD medium refractive index is set to 1.33); complex refractive index of ZnO is taken from ref. [14]. FDTD region is defined by perfectly matched layers (PMLs) in all directions, and the nanosphere is excited by a linearly polarized total-field-scattered-field (TFSF) source from the top (negative $z$-direction, normal incidence). Total scattering cross-section in the 300–1000 nm range is resolved into electric dipole (ED), magnetic dipole (MD), electric quadrupole (EQ) and magnetic quadrupole (MQ) by means of MENP, an open-source MATLAB-based solver for multipole expansion [15]. In Figure 1 we plot such decomposition for nanospheres with radiiuses from 30 nm to 130 nm (with 20 nm step). While MENP method is in principle not restricted to this radii range, we chose it to bring the ZnO resonances in the visible range which is of interest...
for the future experimental work in our laboratory (e.g. excitation at 800 nm, and second harmonic measurements at 400 nm). Each panel in Figure 1 is normalized by the maximum total scattering $\sigma_{sc,max}$ while the scattering efficiency $\eta$ indicates this maximum, normalized to the geometric cross-section. As expected, increasing the nanosphere radius red shifts the spectra and increases $\sigma_{sc,max}$ leading to a peak around 400 nm. For radiiuses $r = 30 - 50$ nm, the ED mode is largely responsible for the scattering, while from $r = 70$ nm, other modes have non-negligible contribution. From $r = 90$ nm, the leading mode at 400 nm is MD mode, having its peak in this range. Interestingly, for $r = 90$ nm, ED and MD overlap around 400 nm, offering the possibility for the first Kerker condition and suppression of backward scattering [2, 16]. We note that the spectral position of the scattering resonances agrees well with the previous experimental results on ZnO nanospheres [17, 18]: in these works, photo-acoustic spectroscopy was applied to measure photothermal response of the sample and extract both absorption and scattering coefficients.

We next investigate the second harmonic far-field distribution if the nanosphere were excited at 800 nm, as in the experimental set-up which we used in previous works treating materials synthetized from [19] or containing ZnO [11]. These simulations are performed using a narrow band 800 nm excitation, with the FDTD continuous wave normalization switched off, to remove the excitation pulse influence on the collection of the results at 400 nm. As we are interested in studying the nanostructure shape influence on the far-field pattern, we approximate the ZnO nonlinearities with a non-dispersive, isotropic material having $\chi^{(2)} = 7.5$ pm/V [20]; this material is a user-defined “chi2” material model in Lumerical, which takes the linear optical properties from already defined ZnO complex refractive index, and adds the nonlinearity by importing a non-zero $\chi^{(2)}$. We underline that this is an approximation which takes into account the shape influences on the second order response, and not the ZnO anisotropy, while highly crystalline ZnO nanoparticles have anisotropic $\chi^{(2)}$ tensor (i.e. c-axis grown ZnO has five nonvanishing tensor elements). In Lumerical, it is currently easy to implement the extension of this method to materials with diagonal anisotropy.

To excite the second harmonic response, we increase the excitation beam amplitude (TFSF source at 800 nm) to $10^{10}$ eV/m. The scattered field distribution is monitored by six monitors surrounding the TFSF source; the global monitor properties are set to override the source limits and detect fields at 400 nm instead. Exciting the different nanospheres at 800 nm, we calculate near-fields in the $xz$-plane, and far-field distributions in the $xy$ and $xz$ planes, emitted by the nanosphere at 400 nm. The nanosphere is excited from the top, and the $XZ$ far-field plane shows fields scattered in the forward and backward directions; the $XY$ far-field plane shows laterally scattered fields, as seen in the inset of Figure 2; this inset also shows the spectrum of a time monitor, clearly showing the excitation spectrum and the nonlinear response generation. We examine dimensions around the Kerker condition; the strongest scattering is in the forward direction, hence we normalize each polar plot with its maximum scattering intensity in the forward direction. From $XZ$ far-field results, we also extract the forward-to-backward ratio, $(F/B)$. For $r = 70$ nm, there is a strong contribution of ED, and the

Figure 1. Multipole decomposition in ZnO nanospheres as a function of radius $r$; each panel is normalized to the maximum of the total scattering, indicated by $\sigma_{sc,max}$, while the scattering efficiency $\eta$ indicates this maximum, normalized to the geometric cross-section.
in-plane scattering is non-negligible, Figure 2a: $F/B$ is 10.2. Increasing the radius to overlap ED and MD, $F/B$ increases to 83.8, and the lateral scattering is much lower, Figure 2b. Finally, at the large radius of $r = 110$ nm, there is a strong forward and negligible lateral emission, Figure 2c, while $F/B$ ratio drops to 34.7. These results show that even a simple nanosphere radius choice tailors the second harmonic field directivity in relation to the modes supported at this wavelength. While the directivity and $F/B$ ratio depend on the nanosphere radius, the total scattered field at 400 nm is the highest for $r = 110$ nm in the forward direction of the XZ plane. Compared to this nanosphere,
nanospheres with \( r = 90 \text{ nm} \) and \( r = 70 \text{ nm} \) scatter 28\% and 5\% in the forward direction, respectively.

### 2.1 Influence of asymmetry

We next investigate how ellipsoid geometry influences radiated second harmonic fields. We define the ellipsoid with three radi \( (r_x, r_y, r_z) \), one of which is set to 200 nm, while the other two are set to 50 nm. The electric field is always linearly polarized in the \( x \)-direction, as in the inset of Figure 3. Figure 3a plots the ellipsoid oriented along \( x \)-direction \( (r_x = 200 \text{ nm}) \); as expected, the strong ED governs the scattering. When electric field is polarized along shorter axis in the \( xy \)-plane, the multipolar analysis gives completely different response, with lower total scattering, Figure 3b. Finally, when long axis of the ellipsoid is parallel to the light propagation, ED and MQ have peaks close to 400 nm, Figure 3c. We next plot the \( XY \) and \( XZ \) second harmonic far-field distribution for the previous configurations, Figure 3d. \( x \)-oriented ellipsoid (long axis oriented in the \( x \)-direction) strongly emits in both \( XY \) and \( XZ \) directions; all polar plots are normalized to its maximum forward emission. \( y \)-oriented ellipsoid is the least efficient, while \( z \)-oriented ellipsoid has negligible backward scattering; these two ellipsoids have negligible lateral emission compared to the \( x \)-oriented one. In Figure 3c, we calculate the average \( XY \) and \( XZ \) emitted second harmonic for the three orientations. There is non-negligible backward and lateral scattering, but the overall far-field response is led by the behavior of the \( x \)-oriented ellipsoid. Understanding the contribution of each orientation to the total scattered field in both linear and nonlinear regime is important if elongated ZnO nanostructures are randomly dispersed in a solution [21].

### 2.2 Influence of chirality

Chirality is a fundamental property of our world; at the nanoscale, chiral objects differently interact with left and right circular polarizations (LCP and RCP, respectively). In nanostructured media, this property tailors linear

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**Figure 4.** Multipole decomposition, second harmonic far-field distribution and nonlinear dissymmetry factor as a function of number of turns of a nanohelix. The inset shows the helix geometry, with linear and nonlinear results for (a) \( N = 0.5 \), (b) \( N = 1 \), and (c) \( N = 1.5 \). Geometric parameters of each helix are \( p = 200 \text{ nm} \), \( d = 100 \text{ nm} \), and \( r = 50 \text{ nm} \). All polar plots are normalized to the maximum forward scattering for RCP excitation.
scattering becomes negligible. Figure 4c shows that MD mode peak red shifts towards 500 nm for $N = 1.5$, but it still has different scattering efficiency between LCP and RCP at 400 nm. This mode then leads to observed chirality in the forward scattering at 400 nm. This is also confirmed by calculating the nonlinear scattered field dissymmetry factors at second harmonic: $g_{SH} = 2 \cdot (I_{RCP,SH} - I_{LCP,SH})/(I_{RCP,SH} + I_{LCP,SH})$, where $I_{RCP,SH}$ and $I_{LCP,SH}$ stand for scattered second harmonic intensity for RCP and LCP excitation, respectively; bottom panels of Figure 4 show $g_{SH}$ as a function of polar angle $\phi$.

We next investigate how the scattering efficiency depends on the loop radius, and how it influences radiation patterns at 400 nm. We keep the following parameters constant: $p = 200$ nm, $N = 1$, $d = 100$ nm, and we change the loop radius $r$. In Figure 4a–4c we plot the scattering efficiencies, as normalized to the geometric cross-section $(r + d/2)^2 \pi$. For $r = 20$ nm, the nanostructure has the shape almost as a rod, and linear multipole decomposition gives extremely low chirality, Figure 5a. Widening the loop to $r = 60$ nm, MD mode peaks around 400 nm, and it has different scattering efficiency for RCP and LCP excitations, Figure 5b. This difference remains for $r = 100$ nm, with the overall scattering efficiency increase, Figure 5c. In Figure 5d we plot the radiation patterns at 400 nm, in $XY$ plane (left) and $XZ$ plane (right), we normalize all graphs to the maximum forward scattering for the most efficient helix, i.e. the one with $r = 100$ nm. Interestingly, this helix has many modes supported at 400 nm, and it provides strong laterally emitted second harmonic at this wavelength.

We first investigate how the number of turns influences lateral and forward scattering, Figure 4; constant geometric parameters are $p = 200$ nm, $r = 50$ nm, and $d = 100$ nm, and each polar plot is normalized to its own maximum forward scattering. When the helix does not have a complete turn, i.e. for $N = 0.5$, difference in the multipolar decomposition is extremely low between RCP and LCP excitations. MD emerges as the only mode with visible difference, and it is stronger for RCP excitation, Figure 4a. At 400 nm, this helix has strong lateral scattering, but, being the Kerker condition close to 400 nm, it has no backward scattering. For $N = 1$, in Figure 4b, difference for LCP and RCP excitation can be appreciated, especially for mode MD. Therefore, in polar plots at 400 nm, we observe difference in forward scattering, which is stronger for RCP excitation at 800 nm. As the number of turns increases, lateral scattering becomes negligible. Figure 4c shows that MD mode peak red shifts towards 500 nm for $N = 1.5$, but it still has different scattering efficiency between LCP and RCP at 400 nm. This mode then leads to observed chirality in the forward scattering at 400 nm. This is also confirmed by calculating the nonlinear scattered field dissymmetry factors at second harmonic: $g_{SH} = 2 \cdot (I_{RCP,SH} - I_{LCP,SH})/(I_{RCP,SH} + I_{LCP,SH})$, where $I_{RCP,SH}$ and $I_{LCP,SH}$ stand for scattered second harmonic intensity for RCP and LCP excitation, respectively; bottom panels of Figure 4 show $g_{SH}$ as a function of polar angle $\phi$.

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In all planes, all helices respond better to RCP incident polarization, and provide lateral scattering comparable to the forward scattering. Accordingly, near field generated around the helices depend on the excitation handedness, as shown in Figure 5e for \( r = 100 \) nm. Therefore, chirality tailors near fields and the far-field directivity at second harmonic wavelengths.

As nanohelices, too, are usually randomly oriented in a liquid, for a complete simulation of chirality, the orientational averaging must be performed, as experimentally shown in reference [36]; this procedure is the subject of future work. Apart from nanohelix geometry [37], a very recent work showed efficient linear chiral response in ZnO crystals synthesized using chiral methionine molecules as symmetry-breaking agents [38]: with chiral response peaking in the blue spectral range, chiral ZnO nanocrystals showed promise for improving surface reactions in photocatalysis. We believe it would be interesting to optimize geometries of such structures according to our simulations, and to measure their nonlinear response. Another interesting field are the cooperative effects in coupled nanostructures; i.e. chiral metamaterials were fabricated from different materials as vertically standing ensembles on substrates [22, 33]. In these cases, the total circular dichroism in the linear range was shown to reach remarkable values as there is no orientational averaging. Therefore, one could study how chirality at fundamental and second harmonic wavelengths tunes the chirality at the emitted second harmonic. Moreover, chirality at the nanoscale can be treated even in achiral samples, where specific modes can lead to enhanced near-field chirality and so-called factor C [2, 39–42]. We predict that the discovered Kerker effect at the second harmonic wavelength can be further combined with the calculations of near-field chirality in solutions of chiral molecules coupled with achiral nanoparticles.

3 Conclusions

We have studied linear and nonlinear optical properties of nanostructures in water by means of FDTD simulations. Starting from the multipole decomposition in semiconductor nanospheres, we have introduced the nonlinear susceptibility. We then excited the nanostructures with strong electric field at 800 nm, and studied near- and far-field distributions emitted at second harmonic wavelength. For ZnO as a test material, nanosphere that supports the first Kerker condition around 400 nm leads to negligible backward scattering of the second harmonic. We further introduced asymmetry and chirality in the nanostructure geometry, and monitored its influence and the second harmonic far-field directivity and dependence on the polarization. We believe that our numerical approach could be a valuable tool for prediction and tailoring of far-field radiation pattern in nonlinear nanophotonics.

Acknowledgments

The authors thank the ENSEMBLE3 Project carried within the Teaming for Excellence Horizon 2020 program of the European Commission (GA No. 857543), and the International Research Agendas Program (MAB/2020/14) of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund and Teaming Horizon 2020 program of the European Commission.

Funding

This research received no external funding.

Conflicts of Interest

The authors declare no conflict of interest.

Data availability statement

Data obtained in this work are not publicly available at this time but may be obtained from the authors upon reasonable request.

Author contribution statement

Conceptualization, E.P.; methodology, E.P. and C.S.; software, E.P. and C.S.; validation, writing – original draft preparation, E.P.; writing – review and editing, C.S.

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