Ensemble and Individual Characterization of the Nonlinear Optical Properties of ZnO and BaTiO3 Nanocrystals

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ABSTRACT: Hyper Rayleigh scattering (HRS) and second harmonic (SH) microscopy were used to study the second order nonlinear optical response of ZnO and BaTiO3 nanocrystals, which have been recently proposed as new markers for bioimaging. HRS, combined with dynamic light scattering, was first used to retrieve hyperpolarizabilities and nonlinear coefficients of both type of nanocrystals. The results indicate that the main contribution to the SH signal is related to the bulk noncentrosymmetric structure of the particles. Successively, we carried out the inspection of individual nanocrystals by SH microscopy, interpreting their response using the nonlinear coefficients deduced from HRS.

1. INTRODUCTION

Recently, there has been a growing interest in fundamental and experimental studies focused on nonlinear optical (NLO) properties of nanoparticles and nanomaterials. This attention is driven by the numerous envisaged applications, exploiting specific or size-dependent NLO properties arising from the low dimensionality of such structures. Among this vast domain, one promising application is the use of NLO nanoparticles as nanoprobes for biomedical imaging. Indeed, several authors have proposed to investigate noncentrosymmetric nanocrystals (NCs) as new contrast agent in second harmonic (SH) microscopy. Some important features result from the combination of SH microscopy and noncentrosymmetric probes, such as coherent optical response, high photostability compared to conventional fluorescent markers as well as wavelength flexibility due to the intrinsic nonresonant nature of second harmonic generation. Such a spectral independence turns out to be of great interest for imaging, since the excitation wavelength can be chosen to minimize both scattering and absorption of the biological sample, increasing the penetration depth of the measurement.

In addition, significant efforts are being made to investigate second order NLO properties of nanoparticles and nanocrystals. Over the past decade, hyper Rayleigh scattering (HRS), initially developed to address dyes hyperpolarizability, has been extended to the characterization of nanoparticles. While several authors have investigated the NLO properties of metallic nanoparticles, less work has been devoted to noncentrosymmetric particles, except for the family of II—VI semiconductor NCs and recently BaTiO3/PbTiO3 NCs. Both types of particles have high hyperpolarizabilities but the physical origin of the second order response is different. For the II—VI semiconductor nanocrystals, it has been shown that this response mainly originates from the bulk noncentrosymmetric structure, except for very small nanostructures (<2–3 nm) where surface SH contribution is not anymore negligible.

From an experimental point of view, HRS has proven to be a useful tool for ensemble measurements whereas SH microscopy is well suited for single nanocrystal characterization. For instance, the SH polarization response of individual NCs has been exploited to retrieve their spatial orientation. Further, several attempts have been made to correlate SH intensity emitted from a nanocrystal with the nonlinear coefficients of the corresponding bulk materials. However, this approach suffers from some experimental complications, as it requires to precisely correlate the NC size and orientation to the SH intensity. Usually, SEM or AFM measurements allow a rapid estimation of the NCs size but their spatial orientation is less trivial to determine. Moreover, sophisticated calculations are necessary to model correctly the NCs SH emission collected by a high numerical aperture objective.

In this study, ensemble measurement (HRS) and individual inspection (SH microscopy) of ZnO and BaTiO3 NCs are described with the aim of quantitatively addressing their NLO properties.
properties. Already proposed as new biomarkers in SH microscopy, hyperpolarizability of both NCs are first examined through a correlation between HRS measurements and dynamic light scattering (DLS). The as-obtained coefficients are then used to interpret the response of individual NCs probed in SH microscopy.

2. EXPERIMENTAL SECTION

Two batches of ZnO nanopowder with different average specified sizes, 20 nm \((\text{ZnO}_{20})\) and 90–200 nm \((\text{ZnO}_{200})\), were purchased from NanoAmor Inc. (Houston). BaTiO3 was supplied by FEE GmbH and was obtained after ball grinding of bulk crystals. X-ray diffraction spectra confirmed the noncentrosymmetric structure of both materials. The tetragonal 4 mm (hexagonal 6 mm) phase was found for BaTiO3 (ZnO) (see Supporting Information).

Several colloidal suspensions were prepared for HRS measurements using the following general procedure: (i) nanopowders are dispersed into water or ethanol with a concentration of 2 mg/mL, (ii) the suspension is sonicated for 5 min at 300 W in continuous mode, and (iii) the solution is left to settle during 5–7 days. A nearly monodisperse colloidal suspension is obtained after the sedimentation of the larger particles and agglomerates occurring during step (iii). Size and particle-size distribution are evaluated by dynamic light scattering (Malvern Zetasizer NanoZS). The NCs concentration is measured after drying the suspension and weighing the residual.

For the HRS characterizations, a YAG laser (Wedge HB, Bright solutions, 1 mJ/1 ns) is focused into a glass cuvette with a 20 cm focal length lens. The scattered radiation is collected perpendicularly to the incident beam by a f/4 lens and measured by a photomultiplier coupled to a boxcar averager. A colored glass filter (short pass) and an interferometric filter (532 nm) are placed in front of the photomultiplier to remove any unwanted light. The fundamental beam polarization is rotated using a half-wave plate. A polarizer can be inserted after the half-wave plate to correlate the bulk nonlinear coefficient of the ZnO or BaTiO3 material to the measured NC hyperpolarizability by using the following expression (see Supporting Information)

\[
\langle \beta_{\text{nc}} \rangle = \langle d \rangle V_{\text{nc}}
\]

where \(\langle d \rangle\) is the average bulk nonlinear coefficient and \(V_{\text{nc}}\) is the NC volume. This expression shows that the HRS signal scales with the square of the volume of the NCs as it has been experimentally reported\(^{12,13,23}\) and recently theoretically demonstrated\(^{24}\) for noncentrosymmetric particles. However, this dependence is only true in the Rayleigh regime, when the NCs size is much smaller than the excitation wavelength. The validity of this assumption will be discussed later.

3. RESULTS AND DISCUSSION

3.1. Hyper Rayleigh Scattering Data Analysis. We start first with a brief description of HRS data analysis, which is adapted from the usual formalism developed to derive nonlinear chromophores hyperpolarizabilities.\(^{21}\) The scattered second harmonic intensity of a suspension of nanoparticles is given by

\[
I_{2\omega} = G(N_{\text{nc}}F_{S}\langle \beta_{\text{nc}}^2 \rangle + N_{\text{nc}}T_{\text{nc}}\langle \beta_{\text{nc}}^2 \rangle)I_{\omega}^2
\]

where \(G\) is an experimental constant, \(N_{\text{nc}}\) is the nanocrystal concentration, and \(\langle \beta_{\text{nc}}^2 \rangle\) is the squared hyperpolarizability averaged over all the possible orientations of the NCs. The subscript \(S\) refers to the solvent. \(F_{S}\) and \(T_{\text{nc}}\) are field factors described below. We use the external reference method with para-nitroaniline (pNA) dissolved in methanol to measure the nanocrystals hyperpolarizability. This method consists in measuring the HRS intensity as a function of the concentration of both nanoparticle suspensions and pNA chromophores solutions. By comparing the slopes \(\alpha_{\text{nc}}\) and \(\alpha_{\text{pNA}}\) of the two measurements, the “per nanocrystal” \(\langle \beta_{\text{nc}} \rangle\) value can be expressed as\(^{21}\)

\[
\langle \beta_{\text{nc}} \rangle = \frac{\alpha_{\text{nc}}F_{\text{pNA}}}{\alpha_{\text{pNA}}T_{\text{nc}}} \langle \beta_{\text{pNA}} \rangle
\]

where \(\beta_{\text{pNA}} = 25.9 \times 10^{-30} \text{ esu}^2\) is the pNA hyperpolarizability in methanol and \(F_{\text{pNA}} = f_{\text{pNA}}^2 f_{2\omega}^2\) is the usual Lorentz–Lorenz correction field factor.\(^{21}\) A reduction field factor, \(T_{\text{nc}}\), is introduced here to better reflect the macroscopic excitation field \(E_{\omega}\) inside the particles. Indeed, for a spherical particle embedded in a homogeneous medium, the internal electric field \(E_{\omega}\) is given by

\[
E_{\omega} = \frac{3n_{s}^2}{2n_{s}^2 + n_{\text{nc}}^2}E_{\text{ext}} = tE_{\text{ext}}
\]

where \(n_{s}\) and \(n_{\text{nc}}\) are the refractive indexes of the medium (i.e., solvent) and the nanoparticles, and \(E_{\text{ext}}\) is the electric field outside the sphere. The reduction field factor can be expressed as\(^{23}\)

\[
T_{\text{nc}} = \frac{I_{\omega}I_{2\omega}}{I_{\omega}^2} = f_{\text{nc}}^2 f_{2\omega}^2
\]

where \(f_{\text{nc}}\) and \(f_{2\omega}\) are the transmission of the NC and the SH wavelengths, respectively. The validity of the previous expression is not always as assumed in literature, where the field factors are often the same for both nanoparticles and solvent or reference molecules.

For NCs with sizes larger than several tens of nanometers, our hypothesis is that the main contribution to the scattered SH intensity originates from the bulk noncentrosymmetric structure, neglecting any possible surface contribution. Therefore, we can correlate the bulk nonlinear coefficient of the ZnO or BaTiO3 material to the measured NC hyperpolarizability by using the following expression (see Supporting Information)

\[
\langle \beta_{\text{nc}} \rangle = \langle d \rangle V_{\text{nc}}
\]

where \(\langle d \rangle\) is the average bulk nonlinear coefficient and \(V_{\text{nc}}\) is the NC volume. This expression shows that the HRS signal scales with the square of the volume of the NCs as it has been experimentally reported\(^{12,13,23}\) and recently theoretically demonstrated\(^{24}\) for noncentrosymmetric particles. However, this dependence is only true in the Rayleigh regime, when the NCs size is much smaller than the excitation wavelength. The validity of this assumption will be discussed later.

3.2. Average Nonlinear Coefficients. An SEM image of ZnO\(_{200}\) raw powder is shown in Figure 2. It is constituted mostly by NCs with size below 300 nm but one can observe some agglomerates and a large size polydispersity. After being sonicated and decanted, the colloidal suspensions of ZnO\(_{200}\) appear slightly translucent and can be used for measurements. For each of the NC types, two sets of independent suspension preparation and analyses have been carried out. For the first suspension of ZnO\(_{200}\), the DLS size distribution by number (inset of Figure 2) reveals an average size of \(D_{n} = 122\) nm with a narrower size dispersion compared to raw powder. The measured weight concentration is 0.13 mg/mL (that is approximately 10% of the initial raw powder concentration) and therefore the maximal
The number density of individual NCs is determined to be about \( N_{nc} = 2.4 \times 10^{10} \text{ cm}^{-3} \).

The mother suspension is then diluted into several samples for which the HRS signal is monitored according to the incident power. HRS increases quadratically with laser intensity, as expected for a second order scattering process (inset of Figure 3). Further, a linear relationship is found between the signal and the nanocrystals concentration, following eq 1. Once these basic relationships are verified, the external reference can be implemented. Table 1 summarizes the results obtained for each kind of crystal. High hyperpolarizabilities, ranging from \( 10^{-23} \) to \( 10^{-25} \) esu, were found according to the NCs type and size. The average nonlinear coefficients were deduced from eq 4.

Note that the crucial step within this analysis is the estimation of the NCs diameter that occurs in the calculation of the number density of NCs and in the determination of the average nonlinear coefficient \( \langle d_{xxx} \rangle \). DLS is well suited for this purpose though it is sensitive to the size of the scattering centers in suspension that might be nanocrystals agglomerates, leading to wrong results. For instance, we observed an increase of the DLS-measured diameter when aging the colloidal suspensions, due to the continuous reagglomeration of the NCs (see Supporting Information). Thus, care has been taken to use only as-prepared supernatant to limit, as much as possible, agglomeration.

Another important limitation of this analysis is related to the polydispersity of the suspensions. Indeed, the larger particles contribute more to the observed signal, as SH is proportional to the square of the volume. Moreover, size dispersion will induce an error in the NCs number density since this parameter is estimated using the weight concentration and the measured NCs diameter. However, as it was stated above, the observed polydispersity can also be due to NCs aggregation and true size dispersion is difficult to evaluate. The ranges of \( \langle \beta_{xxx} \rangle \) and \( \langle d_{xxx} \rangle \) given in Table 1 have been estimated by taking into account the NCs diameters \( D_{a} \) and \( D_{i} \) deduced respectively from the DLS size distribution by number and by intensity (see Supporting Information).

Despite those limitations, the results in Table 1 are very consistent. The discrepancy for the parameter \( \langle d_{xxx} \rangle \) between two sets of measurements is less than 15% for each nanomaterial. We point out here that the relevant intrinsic parameter for a given material is \( \langle d_{xxx} \rangle \), because of the inherent size-dependence of the measured per nanocrystal hyperpolarizability. For example,
The average nonlinear coefficient obtained for ZnO$_{20}$ and ZnO$_{200}$ are very similar, despite their difference in size. This result confirms the assumption of eq 4, which states the proportionality between hyperpolarizability and volume.

This conclusion is also supported by the comparison between the NCs experimental coefficients and the average coefficients deduced from the $d_{ij}$ literature values of bulk crystals. The average bulk coefficients were calculated using eq 6 (see Supporting Information), which will be described hereafter, and are shown in the last column of Table 1. A good agreement is found between the nanocrystals experimental values and the bulk coefficients for the ZnO, which supports the initial assumption of a dominant bulk contribution to the SHI process. For BaTiO$_3$, the comparison is less evident although the order of magnitude is correct.

### Table 1. Measured Hyperpolarizabilities of the Nanocrystals under Study

<table>
<thead>
<tr>
<th>Material</th>
<th>C (mg/mL)</th>
<th>C (cm$^{-3}$)</th>
<th>$D_n$ (nm)</th>
<th>$D_i$ (nm)</th>
<th>$\langle \beta_{xxx} \rangle$ (esu)</th>
<th>$\langle d_{xxx} \rangle$ (pm/V)</th>
<th>$\langle d_{xxx} \rangle_{1B}$ (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO$_{200}$</td>
<td>$1.3 \times 10^{-1}$</td>
<td>$2.4 \times 10^{10}$</td>
<td>122</td>
<td>175</td>
<td>4.4–7.6 $\times 10^{-24}$</td>
<td>1.1–2.0</td>
<td>2.5$^{55}$</td>
</tr>
<tr>
<td>ZnO$_{20}$</td>
<td>$9.8 \times 10^{-2}$</td>
<td>$2.7 \times 10^{11}$</td>
<td>50</td>
<td>90</td>
<td>2.8–6.8 $\times 10^{-25}$</td>
<td>0.7–1.8</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>$1.9 \times 10^{-1}$</td>
<td>$4.0 \times 10^{10}$</td>
<td>115</td>
<td>190</td>
<td>1.0–2.1 $\times 10^{-23}$</td>
<td>2.5–5.3</td>
<td>12.8$^{26}$</td>
</tr>
</tbody>
</table>

* C, nanocrystal weight concentration; $D_n$ and $D_i$ the measured DLS diameter by number and intensity, respectively; $\langle \beta_{xxx} \rangle = (\langle \beta_{xxx}^2 \rangle)^{1/2}$, the orientation average hyperpolarizabilities; $\langle d_{xxx} \rangle$, the average nonlinear coefficient deduced from eq 2 and 4; and $\langle d_{xxx} \rangle_{1B}$, deduced from the bulk literature values of nonlinear coefficients. Note that the $xxx$ subscript refers to the vertical polarization used in our experimental configuration and will be described hereafter.

### Table 2. Measured Depolarization Ratio D and Deduced R Ratio

<table>
<thead>
<tr>
<th>Material</th>
<th>D</th>
<th>$R_{exp}^a$</th>
<th>$R_{lit}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO$_{200}$</td>
<td>0.41</td>
<td>−1.79</td>
<td>−0.095$^{25}$</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>0.36</td>
<td>−0.15</td>
<td>2.55$^{26}$</td>
</tr>
</tbody>
</table>

* Two solutions of $R_{exp}$ are deduced from eq 6. $R_{lit}$ is calculated from the literature bulk $d_{ij}$ values.

### 3.3. Polarization-Resolved HRS

In order to obtain further insight about the NLO properties of these two nanomaterials, we have retrieved their hyperpolarizability tensor components by polarization-resolved hyper Rayleigh scattering. The X-polarized HRS intensity has been measured versus the direction of the incident polarization. The scattered intensity is given by27

$$I_{xx}^X(\omega, \gamma) = \frac{I_{xx}^L}{2} \alpha (\beta_{xxx}^2) \cos^2 \gamma + (\beta_{ZXX}^2) \sin^2 \gamma$$

(5)

where the laboratory frame is defined with X as the vertical direction, Y as the horizontal one, and Z as the beam propagation direction. The angle $\gamma$ is calculated between the X axis and the polarization of the incident beam (Figure 1a). Taking the crystal symmetry and the Kleinman condition into account, both crystals have the same nonvanishing coefficients in the NLO tensor. Moreover, there are only two independent components, $\beta_{31} = \beta_{33} = \beta_{15} = \beta_{24}$ and $\beta_{53}$; therefore the orientation average hyperpolarizabilities are given by

$$\langle \beta_{XXX}^2 \rangle = \beta_{33}^2 \left( \frac{1}{7} + \frac{12}{35} R + \frac{24}{35} R^2 \right)$$

and

$$\langle \beta_{ZXX}^2 \rangle = \beta_{33}^2 \left( \frac{4}{35} R + \frac{4}{21} R^2 \right)$$

(6)

with $R = \beta_{31}/\beta_{33}$

The HRS polarization response of ZnO$_{200}$ and BaTiO$_3$ are shown in Figure 4. The experimental data points have been fitted according to eq 5. The corresponding depolarization ratios, $D = \langle \beta_{ZXX}^2 \rangle / \langle \beta_{XXX}^2 \rangle$, are 0.41 for ZnO and 0.36 for BaTiO$_3$. These experimental ratios provide two possible solutions for $R = \beta_{31}/\beta_{33}$ (Table 2). One of the solutions for ZnO NCs, $R = −0.19$, is actually close to the bulk value, but for BaTiO$_3$ the two solutions differ from the literature results. This comparison with the published values of NLO tensors should be set in the context of a large discrepancy between the values determined for ZnO by different authors, and the lack of any recent measurement for BaTiO$_3$. However, the observed deviation for BaTiO$_3$ is still unclear and may be due to larger experimental uncertainties eventually related to an higher polydispersity inherent to the
sample preparation. Additionally, even if our main assumption states that the bulk contribution to the HRS signal is the dominant one, the observed discrepancy might point to the necessity to refine the model of NLO response, including, for example, the nanoparticle shape effect, as discussed in Section 3.4.

To sum-up this section on HRS measurements, we have developed a detailed approach for the analysis of noncentrosymmetric nanocrystals. Experimental measurements were found to be reproducible but uncertainties in the quantitative evaluation of the independent NLO coefficients are still large due to the size and shape polydispersities of available nanomaterials. Future investigations on NCs suspensions with reduced polydispersities appear necessary to avoid the above-mentioned limitation.

Furthermore, we highlight two caveats for the application of this approach. On the contrary, when using larger noncentrosymmetric nanoparticles under study, and (4) a poor modeling of the polarization distortions by the optical apparatus. Concerning KTP nanocrystals (>200 nm diameter) for the sake of comparison, we saw a clear enhancement of the forward intensity. Incidentally, the experimental determination of second harmonic scattering behavior outside the Rayleigh regime is a promising topic for future work, even if it is beyond the scope of this paper.

3.4. Second Harmonic Generation Microscopy. After the ensemble measurements, the individual nanocrystals nonlinear properties were studied by SH microscopy. Samples were prepared by drying a drop of the previously described colloidal suspensions on a standard microscope glass substrate. The samples were first analyzed by AFM, for localizing single NCs and measuring their sizes, eliminating larger clusters from the subsequent analysis. The same samples were then transferred to the optical microscope, where the images of the same regions studied by AFM where acquired by epifocusing the SH intensity as a function of the microscope scanner position. As reported in Figure 5a, we observe a perfect correlation between the AFM and SH images.

For each sample (ZnO or BaTiO3), the polarization response of several NCs were then acquired (Figure 5b,c) by placing thanks to the scanner the selected NC in the objective focus, and then recording the SH intensity as a function of the excitation polarization for the two orthogonal polarization of the detection analyzer. To fit these traces, we have first implemented a simple model. The incident field, polarized in the γ direction with respect to the X axis, is described using two in-plane components, $E_{\gamma} = E_{\omega} \cos(\gamma)$ and $E_{\omega} = E_{\omega} \sin(\gamma)$. The collected SH intensity is then considered to be proportional to the square of the nonlinear polarization, calculated using the crystal nonlinear coefficients $d_j$ and the NCs orientation defined by the Euler angles. Contrary to the Euler angles, which are let free to vary in the fitting procedure, the $d_j$ elements are kept fixed at the values previously determined by HRS. The results of the fitting procedure are generally satisfactory for both NCs type. Note that for BaTiO3, the $d_j$ elements from the literature have also been used ($d_{11}/d_{33} = 2.55$ instead of $d_{11}/d_{33} = -2.72$). The fitting quality was neither significantly improved nor deteriorated.

However, we remark that for a significant fraction of the individual NCs analyzed, we did not succeed in obtaining an adequate agreement with the experimental response. We have therefore implemented a more sophisticated modeling procedure, accounting for the polarization distortions introduced by the optical apparatus as described in ref 28. Briefly, the procedure consists in modifying the incident field description using ellipticity and dichroism as additional input parameters, independently measured. Moreover, we have included in the modeling the effect of the high numerical aperture objective on the collection of the SH. The detected intensity is obtained by integrating the square of the second harmonic field radiated by the induced nonlinear dipole over the cone angle defined by the objective aperture. However, we did not find any substantial improvement in the fits agreement by this more elaborated approach.

This difficulty can be ascribed to several factors: (1) the large parameter space required for the computational fitting procedure, resulting in a critical sensitivity to the initial guesses, (2) a dependence of the $d_j$ element on the excitation wavelength that for microscopy differs from that of the HRS measurements (800 and 1064 nm, respectively), (3) a remaining agglomeration in the nanoparticles under study, and (4) a poor modeling of the polarization distortions by the optical apparatus.
the last statement, as we have just mentioned, we have imple-
mented the state-of-the-art modeling of the polarization re-
sponse of the optical setup and not much improvement seems
possible. Moreover, all these possible explanations do not
account for the fact that we are able to obtain good agreement
for most of the NCs. More likely, the discrepancies we observe
are related to the specific shape of individual NCs (the so-called
form factor): it has been reported, for instance, that for high
aspect-ratio nanocylinders the nonlinear polarization is strongly
modulated as a function of the angle between the incident
field E vector and the cylinder major axis. 30 Even though all
the dimensions of the NCs under study here are smaller than the
fundamental and the SH wavelength, it would not be surprising
to observe shape-sensitive depolarization effects for highly
anisotropic particles like the ones shown in the SEM picture
in Figure 4. These effects likely average out in the ensemble
HRS measurements, while remaining significant for microscopy,
determining both a particle’s shape and particle’s orientation
dependence not included in our present polarization response model.

Finally, we compared the SH intensities emitted by isolated
nanocrystals with the one obtained with a bulk lithium niobate
crystal, which was chosen as reference material. A priori, this
procedure should allow retrieving the absolute values of NLO
coefficients, provided that the NC orientation is precisely
determined. The detected intensity can be expressed as 31
$I_{X,Y} = AV^2 f_{X,Y}(d_{ij},\theta,\phi,\psi)$, where $A$ is a proportionality constant
dependent on the experimental signal collection conditions, and $V$
is either the NC volume, independently determined by AFM
assuming a spherical particle shape, or for the bulk crystal
measurements the nonlinear focal volume. This comparison
did not yield the expected results for both the materials under
study. Indeed, we found (i) a large spreading of the results when
repeating the procedure on different NCs, probably resulting
from an important error in the determination of the off-plane
Euler angle $\theta$; 32 as the parameter $A$ and $\theta$ are strongly correlated and
(ii) very large values, greatly exceeding the NLO bulk
coefficients. Concerning the last statement, we believe that an
elaborated model must be used for a complete analysis, account-
ing for tight focused excitation and coherent superposition
effects. 19,31 These effects are particularly significant for the bulk
crystal in a backward configuration and lead to an inaccurate
estimation of the nonlinear focal volume. Although elaborated
models can be implemented, our purpose here is just to point out
that an absolute determination of NLO coefficients relying
exclusively on SH microscopy is not a straightforward procedure.

4. CONCLUSIONS

In this study, we developed a detailed approach for HRS
characterization of ZnO and BaTiO3 NCs, among the most
promising SH nanoprobes for imaging. We also proposed a
specific data analysis which yields the nonlinear coefficients of
the NCs, allowing a straight comparison with the values of the
second order NLO properties of these NCs originate from the bulk noncen-
trosymmetric structure and thus, that the SH intensity is propor-
tional to the square of their volume. Moreover, polarization
resolved HRS was used to retrieve NLO tensor coefficients that
have been fed as input parameters to interpret the SH
microscopy response of particles of both nanomaterials. We
show that the interpretation of second harmonic intensity
collected by the microscope is not straightforward and demon-
strate that HRS is the adequate technique in order to retrieve
reliable NCs NLO properties. This work also points out that
progress in synthesis procedures is of key importance for the
development and future use of these SH nanomaterials.

ASSOCIATED CONTENT

Supporting Information. X-ray diffraction studies, relation-
ship between hyperpolarizabilities and NLO coefficients, DLS and HRS measurements when aging a colloidal suspension,
estimation of the hyperpolarizabilities and NLO coefficients
uncertainties, calculation of the average bulk coefficient, and
polarization response of bulk BaTiO3 crystal. This material is
available free of charge via the Internet at http://pubs.acs.org.

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