Subwavelength vaterite spherulite scattering properties in optical region

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Abstract. Vaterite is a very promising material for biological applications, but its electromagnetic properties have not been studied well enough. In this work we for the first time introduce multipole decompositions of subwavelength nanoparticles for dark field microscopy in optical range.

1. Introduction:
Nowadays, all-dielectric photonics is a perspective field of modern researches [1,2]. Recent works show a high potential for light manipulation and control of subwavelength scatterers for different scales [3,4]. The low losses in optical region, make dielectric scatterers an alternative to plasmonic ones, which applications are often limited by Ohmic losses. Moreover, it has been shown that both electric and magnetic multipole resonances may be excited if the scatterer permittivity is big enough [5–7].
The practical applications of dielectrics in nanophotonics are widespread and manifold, for example, metasurfaces for photovoltaics [8–13], cloaking [14,15], enhancement of nonlinearity [16,17], bianisotropy [18–21], etc.
Dielectrics (e.g. silica, calcium carbonate, calcium phosphate etc) are in a high demand for biophotonic applications [22,23]. One of the very promising materials is a modification of calcium carbonate so-called vaterite. Vaterite is a porous structure material consisting of single uniaxial nanocrystals aligned with confocal hyperbolas. It has promising applications in drug delivery [24], real time imaging processes [25], optical tweezers [26].

In this work, we investigate the vaterite spherulite scattering properties in the optical range. To describe vaterite in optical range we assumed that the refractive index does not change with the wavelength. Variation of the vaterite refractive index \( n \approx 1.486 - 1.658 \) is connected with anisotropy and depends only on the spatial distribution of uniaxial crystals of which it consists [27].
Thus, geometry and the low refractive index of the vaterite sphere define low-Q factor subwavelength resonator and subtle optical responses. In our model TE polarized plane incident at 65[deg] to a substrate normal. The substrate is the optical glass with refractive index n=1.46. We assume that for possible experiment solid angle for collecting light is pi/4 steradian.
Figure 1. Total scattering efficiency of vaterite spherulite with R=220nm placed on a glass substrate with n=1.46 for TE polarized wave incident to the substrate at 65[deg] (a). Multipole decomposition of a backward scattered light in a solid angle of pi/4 steradian (b). Electric quadrupole and magnetic dipole do not produce an equal contribution to the backscattering, therefore electric dipole and magnetic quadrupole contributions dominate in short wavelength due to an orientation of their radiation patterns.

Figure 1(a) the scattering efficiency for Cartesian multipole decomposition [28] for vaterite spherulite approximated with a sphere with nm R=220nm. In the long wavelength range of 550-880 nm, the scattering efficiency is defined by slow varying electric and magnetic dipoles, electric quadrupole. The magnetic dipole in this range has a peak of scattering efficiency. Besides the slow raise of the electric quadrupole and decrease of the magnetic dipole in short wavelength range of 450 and 550 nm, electric dipole and magnetic quadrupoles resonances have overlapped peaks.

For low refractive index the contribution of higher order multipoles, such as electric and magnetic octupole moments should be considered. In the short wavelength region it leads to the excitation of a magnetic octupole moment and higher multipoles. As soon as the magnetic octupole gives sensible contribution to the multipole decomposition spectra the mismatch of the multipole decomposition with the total scattering indicates necessity to include a second order toroidal magnetic dipole and a second toroidal electric quadrupole. Unfortunately, those high order toroidal moments are not included in the 5th order irreducible Cartesian multipole decomposition and this limitation should be taken into account.

Scattered fields observed for a single nanoparticles in optical region cannot be measured in full solid angle, due to numerical aperture of light collecting optics. The multipole decomposition of a scattering efficiency (for full solid angle [28] Equation 25) calculated for a solid angle $Q_{\text{scat}}^{NA}$ can be found from:

$$Q_{\text{scat}}^{NA} = \frac{1}{|E_{\text{inc}}|^2} \int_0^{\pi/2} \int_0^{2\pi} |E_{\text{scat}}|^2 \sin(\theta) \ d\phi \ d\theta,$$  \hspace{1cm} (1)

where $E_{\text{scat}}$ is a scattered E-field in the representation of irreducible Cartesian multipoles (Equation 6 in [28]), $|E_{\text{inc}}|$ is an amplitude of incident field, angles $\theta'$ and $\theta''$ define position and light collected an aperture for dark-field calculations in spherical coordinates.

Figure 1(b) shows the scattering efficiency for backward scattering or $\theta'=0$ and $\theta''=\pi/8$ in Equation (1). TE polarized incident wave have pronounced broadband peak of overlapped magnetic
quadrupole and electric dipole at 490 nm. Also it shows dominating and broadband response of magnetic dipole in the long wavelength region.

Comparison of figure 1 panels (a) and (b) shows suppression of magnetic dipole and electric dipole contributions in the short wavelength region for the \( Q_{\text{scat}}^{NA} \). At the same time full scattering reveals almost equivalent amplitudes of first 4 multipoles in spectrum. Thus, it experiences generalized Kerker condition [29,30].

**Conclusion:**
In this work, we first time demonstrate multipole decomposition of vaterite subwavelength nanostructures for dark-field optical microscopy. Vaterite low refractive index defines subtle optical resonances over the whole optical region. The peculiarities of the system and multipole responses for total scattering and light collected in a solid angle are discussed. The obtained multipole decomposition may be used for scattered light manipulation and control, for improvement vaterite structures imaging, trapping, etc.

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