

In-situ Surface Characterization of Nano- and Microparticles by Optical Second Harmonic Generation

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ABSTRACT

Nonlinear optical spectroscopic techniques, namely Second Harmonic Generation (SHG) spectroscopy and Sum Frequency Generation (SFG), are highly interface sensitive and can be used to obtain information exclusively from the surface of particles. Second Harmonic Generation (SHG) has proven to be a versatile technique that can be used to probe different kinds of surface properties of dispersed particle systems in in-situ. Prominent examples are the direct study of molecular adsorption at the surface of particles and the determination of surface potentials of nano- and microparticles. However, in most of these studies well-defined spherical and monodisperse particles with low number densities were used. Here we demonstrate the application of the SHG technique for the study of more complex and technically relevant particle systems. We discuss the influence of particle concentration and particle size distribution. Moreover, we apply a novel nonlinear Mie Model that is capable to simulate the SH scattering from the surface of spherical particles and we show that the model can be used to extract information about molecules at the particle liquid interface.

Keywords: surface characterization, nonlinear Mie model, Second Harmonic Generation, optics, nanoparticles

1 INTRODUCTION

The macroscopic properties of particulate systems are mostly controlled by microscopic properties of the particle interfaces. Therefore in nanotechnology it is not only necessary to get information on size and shape of particles but also on additional surface properties as charge, surface structure and interface molecules.

There are several optical techniques as static and dynamic light scattering or image analysis which can be used to get information on size and shape and number densities of particles in suspensions and powders and which can also be used for online measurements during production and processing of particles. Methods for the in-line characterization of particle surfaces are rare. Most surface analytical techniques cannot be used directly in the

process since they require often high vacuum, special preparation techniques or long measuring times.

Nonlinear optics opens the possibility to study embedded surfaces in-situ and in real time. Second Harmonic Generation (SHG) Spectroscopy is a well established technique for the investigation of planar interfaces [1–3]. Recently, it has also been applied to study the surface properties of colloidal interfaces [4]. Since then a lot of different particulate systems have been studied by nonlinear optical spectroscopy [5–15]. The Second Harmonic light is scattered at half the wavelength of the light which is used for excitation. In contrast to linear optical methods, where the separation of bulk and surface signals is often difficult if not impossible, second order nonlinear effects are exclusively surface sensitive. The signal generation depends on the nonlinear susceptibility $\chi^{(2)}$ of the system which vanishes for centrosymmetric materials. Interfaces between two such materials represent a symmetry break and do therefore possess a nonlinear surface susceptibility, which depends on the number of surface molecules, their orientation and local electromagnetic fields. The method can in principle be applied to any optically accessible interface between two centrosymmetric bulk media. However, a factor that can hinder the application of SHG is that many molecules and interfaces have only a weak nonlinear susceptibility $\chi^{(2)}$ and therefore their Second Harmonic (SH) signal can be too low to be detected [12]. The particle sizes, particle concentration as well as the absorption of the media and the particles also have a strong effect on the total detectable Second Harmonic signal intensity [16].

For the application of SHG to more complex and technically relevant systems the influence of the detection geometry and the dependence of the SH scattering process on particle concentration and particle size distribution have to be elucidated. Therefore we have performed systematic studies with mixtures of monodisperse polystyrene particles in aqueous suspension and have compared the generated signal intensities quantitatively [17]. The applicability of the SHG technique for the study of technical relevant particles is demonstrated by experiments with ground TiO₂ particles.

Further, we have used angle-resolved SHG to derive additional information about surface molecules that are not

accessible with conventional experimental transmission setups. A new nonlinear Mie theory is applied to simulate the SH scattering from individual molecules with arbitrary orientation that are located at the surface of spherical particles. Using this nonlinear Mie model we are able to derive additional information about molecules at the particle liquid interface [18].

2 EXPERIMENTAL SECTION

The experimental transmission setup used to study the influence of particle size distribution and to derive the surface potential of TiO_2 particles is shown in Figure 1.

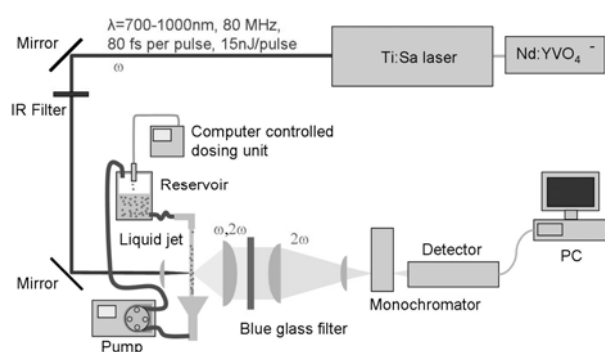


Figure 1: Schematic SHG transmission setup.

For the excitation of the SHG signals a pulsed Ti:Sa femtosecond laser with a pulse length of about 80 fs is used. The wavelength can be varied between 700 and 1000 nm. The beam is focused into the sample where the SHG signal is generated. With a second lens after the probe the scattered light is collected. A blue color filter that transmits only light shorter than 650 nm is used to block the transmitted and linear scattered laser light. The filtered light is then focused into the slit of a monochromator for a further separation of the SHG signal from other background radiation as two photon fluorescence. The SHG light is detected by a photomultiplier tube and recorded by a computer. For the measurements we use either a quartz cuvette with an inner diameter of 2 mm of a flow cell, consisting of a reservoir that contains the sample and an outlet tubing. A laminar liquid jet is formed which is collected with a funnel and is pumped back to the reservoir by a peristaltic pump. The SH signal is generated by a laser beam the laser beam that is focused inside the laminar jet. By the continuous flow of the suspension local heating of the sample and temporal variations of the solid concentration due to sedimentation are avoided. A computer controlled dosing unit was used to systematically vary the electrolyte concentration of the suspension by adding a 100 mM NaCl solution.

The experimental setup for the angle-resolved SHG measurements is shown in Fig. 2.

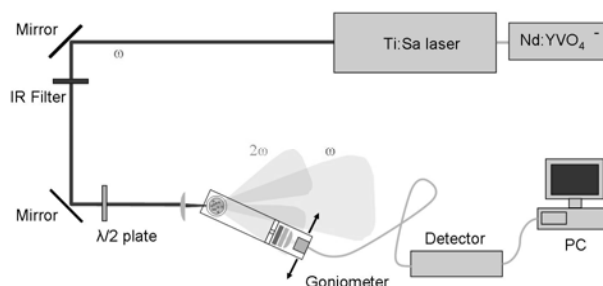


Figure 2: Schematic SHG setup for angle resolved experiments.

In contrast to the transmission setup, the optics for the detection of the SH light are mounted on a computer controlled pivot arm. For the angle resolved measurements a cylindrical cuvettes with an inner diameter of 3.5 mm is used. The angular resolution of about 1.4° of the goniometer setup is confined by a spherical aperture in front of the detector head.

3 RESULTS AND DISCUSSION

3.1 Influence of Particle Concentration and Particle Size Distribution

In Fig. 3 the characteristic dependence of the detected SH intensity in forward direction on the particle number density for monodisperse 770 nm polystyrene particles is shown. At low number densities, the SH signal increases linearly with the number of the particles. At a number density of about $1.25 \cdot 10^9$ particles / ml a maximum occurs and at even higher particle concentrations the SH signal in transmission decreases. In principle this decline could be caused by two different processes. The first is scattering and absorption of the laser light and the generated SH light by the particles in the suspension. The second process is interference of the SH signals from individual particles at high particle densities.

When the laser beam passes through the cuvette a part of the light is scattered and absorbed by particles in the suspension. The total intensity of the generated SH signal is proportional to the square of the intensity of the incoming laser beam. Thus, most of the SH signal is generated in the focal region which is schematically indicated in Fig. 4. Laser light that is absorbed before the focus region as well as light that is scattered in a way that it not reaches the focus region causes a decrease of the generated SH signal. On the other hand, SH light that is generated at the surface of the particles in the focus region is also scattered and absorbed by particles on the way to the detector. In a transmission setup the light is typically collected with a large solid angle of $40^\circ - 50^\circ$. Thus the intensity of the generated SH signal that reaches the detector depends on

the detection geometry as well as on the angular dependent Mie scattering by the particles.

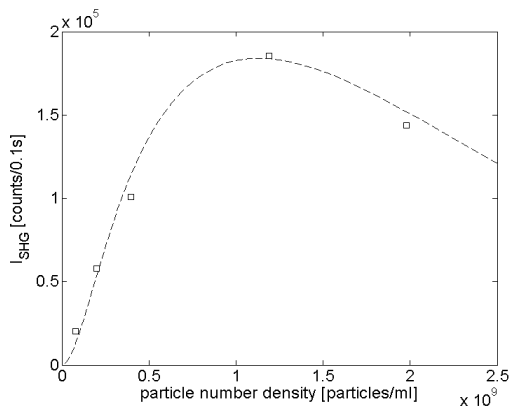


Figure 3: Dependence of the detected SH intensity in forward direction on the particle number density of 770 nm polystyrene particles with surface adsorbed malachite green

However, the decrease in the transmitted SH intensity with higher particles densities could also be caused by interference. The coherence length of the SHG process is in the order of micrometers. If the distance between individual particles is smaller than the coherence length for SHG, than the individual signals from individual particles do not simply add up, but interfere with each other and a nonlinear dependence between the generated SH signal and the particle density is expected. If this is the case, the total SH signal from particle samples with a wide size distribution can not be described as sum of the SH signals from the individual particles.

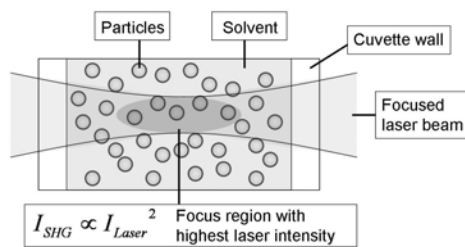


Figure 4: Schematic illustration of the focused laser beam inside the particle suspension

To determine the dominating mechanism that causes the decrease of the SHG signal in transmission at high particle concentrations, different samples of monodisperse polystyrene (PS) particles were mixed together and the intensities of the transmitted SH light within a solid angle about 48° were measured. The diameter of the PS particles used for these experiments was between 50 nm and 1.1 μm. The experiments were performed at different particles densities with solid concentrations ranging from 0.01 to 0.5 w/v%. For all samples a nonlinear relation between SH signal and particle density was observed at high particle concentrations. However, we found a linear dependence of

the total SH signal intensity on the mixing ratio of smaller and larger polystyrene particles as long as the extinction of the samples was comparable for all samples. From our result we conclude, that the decrease of the SH signal at high particle densities is mainly caused by absorption and scattering. This suggests, that the total SH signal intensity can also be used for the quantitative study of surface processes of polydisperse and high concentrated particle samples.

3.2 Study of technical particle systems

To demonstrate the applicability of SH light scattering for the quantitative study of technical relevant particles we have analyzed the SH signal from anatase TiO₂ particles with a mean diameter $x_{50,3}$ of 370 nm in water at different electrolyte concentrations. In Fig. 5 a scanning electron microscope (SEM) image of a dry particle sample on a silicon wafer is shown.

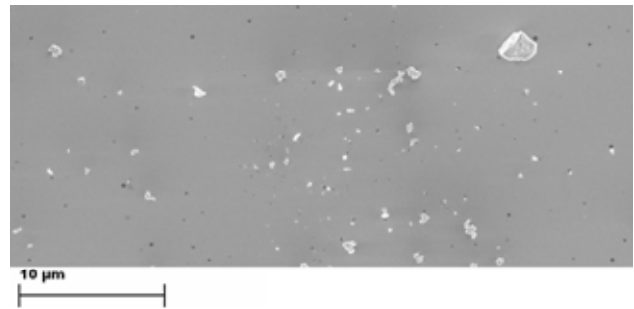


Figure 5: SEM image of a dry TiO₂ particle sample

As the particles were produced by a grinding process the particles are non-spherical and exhibit a wide size distribution as can be seen from the representative probe in Fig. 5. The SH signal from these particles consists of two source terms that interfere with each other. One of these is attributed to a contribution from the bulk of the particles. The magnitude of this term is not depending on the electrolyte concentration of the surrounding liquid. The other term is attributed to a layer of oriented interfacial water. The static electric field of the negative charges at the particle surface induces the orientation of the dipolar water molecules near the particle-liquid interface. In the presence of ions in the suspension an electrical double layer is formed and the negative surface charge is screened by positive counter ions. Thus, the penetration depth of the static electric field and the degree of orientation of the water molecules depends on the electrolyte concentration [19]. This correlation can be used to estimate the SH surface potential of the particles by fitting the dependence of the SH signal intensity on the electrolyte concentration with the Gouy Chapman double layer model [20]. In titration experiments with TiO₂ particles at different NaCl concentrations we found a SH surface potential of -67 mV at 10 mM NaCl and neutral pH. Using laser Doppler electrophoresis a zeta potential of -43 mV was measured for

the same sample. This discrepancy between the SH surface potential and the zetapotential can be explained by the difference in the measurement principles. The zetapotential is a measure for the potential in the slipping plane whereas the SH surface potential is a measure for the orientation of the interfacial water layer which is closer to the particle surface than the slipping plane. Thus SHG measurements provide a potential that can be expected to be closer to the real surface potential than the commonly used zetapotential.

3.3 Application of Nonlinear Mie theory

In the previous mentioned applications of SH light scattering only the total SH signal intensity within a large solid angle was measured. However, it has been shown that SH light scattering from spherical particles exhibits distinct angular scattering profiles that differ significantly from the profiles of linear light scattering. We have developed a nonlinear Mie model that is capable to calculate SH light scattering from molecules at the surface of spherical particles [18]. The model can be applied to quantitatively analyze the nonlinear response of the interfacial molecule layer, allows us to derive information about the density and order of the surface molecules and to determine the dominating components of the surface susceptibility.

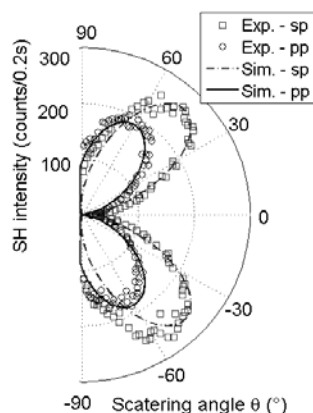


Figure.6: Comparison of experimental and simulated SH scattering profiles for a 200 nm PS particle with adsorbed MG at the surface

The experimental scattering profiles from a suspension of 200 nm PS particles with surface adsorbed MG molecules as well as respective simulations are shown in Fig. 6. A good agreement between simulations and experiment is found indicating that the nonlinear Mie model can be applied for the quantitative analysis of angular-resolved SH experiments with different types of colloidal particles.

4 CONCLUSION

We could show that the SH light scattering can be applied for the in situ study of surface properties of polydisperse particles in aqueous suspension. Furthermore a nonlinear Mie theory was applied to quantitatively analyze the angular SH scattering profiles from suspensions of spherical particles.

ACKNOWLEDGMENT

The authors gratefully acknowledge the funding of the German Research Council (DFG), which, within the framework of its 'Excellence Initiative' supports the Cluster of Excellence 'Engineering of Advanced Materials' (www.eam.uni-erlangen.de) and the Erlangen Graduate School in Advanced Optical Technologies (SAOT) at the University of Erlangen-Nuremberg.

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