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Short communication

Improved non-invasive Optical Coherence Tomography detection of different engineered nanoparticles in food-mimicking matrices

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ABSTRACT

Food industry and regulators require fast and reliable analytical methods for quality control. This especially counts for the detection of engineered nanomaterials (ENMs) in food products. Respective EU regulation is in force, but the development of appropriate methods is still underway. This paper updates the scope of Optical Coherence Tomography (OCT) for ENM/food matrix analysis. A range of nanomaterials and composites – Au@SiO_2, Ag, Ag@SiO_2 and SiO_2 – in a simplified food matrix was investigated. The earlier finding of linear dependencies between concentration in the dispersion and light responses could be reproduced. Being able to analyse non-invasively for a relevant industrial compound such as SiO_2, makes OCT an excellent candidate for screening purposes.

1. Introduction

Recent years have seen an increase in the use of engineered nanomaterials (ENMs) in many fields, amongst them food and nutrition. While the potential benefits of such particles are beyond any doubt, the impact of ENMs on customers health and safety is not clear (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2012). To enforce the consumer's "right to know", the European Union has passed legislation on the labelling of food products (Food Regulation (EU) 1169/2011). The regulation demands a statement whether engineered nanomaterials (ENMs) have been used as food additives. Implementation of this legislation will eventually require detection and quantification of nanoparticles in food. In recent years, several methods have been published for the detection of e.g. Ag or silica nanoparticles in food, e.g. by separation with field-flow fractionation and subsequent quantification by conventional or single-particle ICP-MS (Loeschner et al., 2013) or multi-angle light scattering and ICP-MS (Wagner et al., 2015) or direct detection by electron microscopy without fractionation (Tiede, Dudkiewicz, Boxall, & Lewis, 2015) or surface plasmon resonance (Raz, Leontaridou, Bremer, Peters, & Weigel, 2012). A general review of techniques for detection, characterization and quantification of inorganic engineered nanomaterials in complex matrices has recently been published by Laborda and colleagues (Laborda et al., 2016). However, these methods usually involve extensive sample preparation, which is not only time consuming but can also have a high impact on measuring uncertainties (Dudkiewicz et al., 2015). Non-invasive methods leave the specimen unchanged and hence reduce the measurement bias from matrix destruction, the time consumption for data generation and imaging is minimal compared to destructive methods.

Optical Coherence Tomography (OCT) is an established interferometric imaging technique in medical diagnostics. Three-dimensional imaging with a high-resolution of better 10 μm laterals, as well as in depth is state of the art. In Fourier domain OCT, the principle setup is an interferometer. Broadband near-infrared light is split into a reference beam and a sample beam. Light, which is back-reflected or back scattered interferes with the returning reference light and is spectrally resolved. The detected interference spectra encode the entire depth information. One depth profile of reflectivity, referred to as A-scan, can be calculated from one single

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interference spectrum via Fourier-transformation. Since OCT is sensitive to scattering and back reflecting structures, it is considered potentially appropriate for detecting nanoparticles in solid matrices. The hypothesiszed utilization is to identify suspicious samples or for calibration in the regulatory and quality application (Grombe, 2012).

The project builds on a previous study (Grombe et al., 2014), dealing with well-defined gold nanorods (AuNR) and investigates whether OCT is capable of analysing a wider range of nanoparticle species. Polymer-protected silver, as well as silica shelled-gold and silver nanomaterials, were incorporated. The silver nanomaterials differ in geometry from gold but have optical activity, similarly matching the NIR light source of OCT. Silica nanoparticles were added to the pool as they are part of the food additive E551 (Dekkers et al., 2011). However, as their optical properties vary from those of the metal nanomaterials, it was unclear how such change influences the detection and quantification capabilities of OCT.

This paper presents data on additional nanoparticles to investigate further the applicability of OCT, using four different kinds of metal-silica nanoparticles dispersed in a polymeric carrier at four concentrations.

The ENMs have been embedded in polymeric thin films of a food additive (PVP, E1201), which serves as a model system for a simplified food matrix. This will provide data, unbiased from complex texture and composition.

The previous study suggested that the limit of detection (LOD) could be improved by changing the acquisition and averaging procedure. This paper, therefore, also reports on the improvement of the OCT imaging following this route.

2. Materials and methods

2.1. Sample preparation

Table 1 gives an overview of the used ENP dispersions, source and particle characteristics. Polyvinylpyrrolidone (PVP) was used as ENP stabilizer and a film forming agent.

2.1.1. Coating formulation

An aqueous Polyvinylpyrrolidone (PVP K90, VWR International, Belgium), solution (5 g/kg) was obtained by adding 0.5 g PVP in 100 g of ultrapure water (MilliQ, 18 MΩ cm^{-1}) followed by shaking until a clear solution was obtained. It was used to formulate dispersions S1–S3 (Table 1) having nanoparticle concentrations of c_1 = 20 mg/L, c_2 = 2 mg/L, c_3 = 0.2 mg/L, c_4 = 0.02 mg/L, PVP (blank): c = 0 mg/L. The concentration of PVP with a nanoparticle concentration series is constant: 0.5% m/m PVP solutions were taken to produce the single dispersions. PVP blanks were diluted accordingly. Silica/PVP containing samples (Entry S4, Table 1) were produced by adding PVP to the silica dispersion to achieve 50 g/kg on PVP. The resulting clear viscous solution was diluted with ultrapure water (MilliQ, 18 MΩ cm^{-1}) to reach c_1–c_4. All produced dispersion of S1–S4 had a pH of 6–7.

2.1.2. Preparation of test specimens

Microscopy slides (75 × 25 × 1 mm^3) were cleaned, dried and wetted with the respective coating solutions to produce a macroscopically homogeneous film. After evaporation of the solvent, the specimens were put in sachets, and air tight sealed.

2.2. OCT Setup and image acquisition

The utilized OCT system is a self-built spectral domain OCT system providing an A-scan rate of 11.9 kHz. The interference spectra are measured using a spectrometer unit. A super-luminescence diode (SLD) with a center wavelength at 880 nm and a total spectral width of 130 nm was used as a broadband light source. The depth resolution (axial resolution) was 6.4 μm and the lateral resolution in the focus was 6.7 μm. The sensitivity was measured to be 102 dB. The principle scheme of the OCT-system is depicted in Fig. 1. The light of the SLD was guided through a fiber-optic setup, mainly via a fiber-optic coupler, to the scanner head, which contains a modified Michelson interferometer and two galvanometric scanners for the beam deflection in both lateral dimensions. The optical power of the light penetrating the sample was below 2 mW. Further details about the OCT-system have recently been published (Burkhardt, Walther, Cimalla, Mehner, & Koch, 2011).

The background noise impacts the LOD. It was necessary to average complex A-scans at fixed lateral position to reduce the noise level. Because the phase of the noise is random, the noise level can be decreased significantly by averaging while keeping the sample signal nearly constant. A detailed explanation of the advantage of complex averaging over standard averaging can be found elsewhere (Szkulmowski & Wojtkowski, 2013).

In the following evaluation, M-scans have been acquired, each consisting of 320 depth scans at a fixed lateral position. 320 of such M-scans at adjacent transverse positions were recorded, having a total data size of 800 MB. After changing the lateral position of adjacent M–scans, the first 120 A-scans were neglected to achieve a stable phase signal. The remaining 200 A-scans are used for the calculation of a complex averaged A-scan. In the following, a single

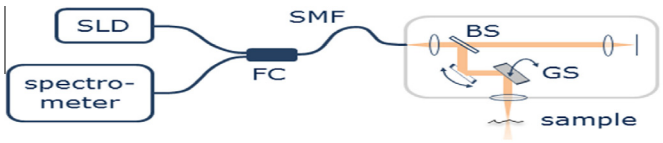

Fig. 1. Principle sketch of the OCT-system. Abbreviations: BS: beam splitter, FC: fiber optic coupler, GS: galvanometric scanner, SLD: superluminescence diode, SMF: single-mode fiber.

Table 1
The source and the respective particle characteristics of the ENP dispersions to produce the coating formulations are given; AuNR – gold nanorods, AgNT– silver nanotriangles.

Entry	ENP dispersions	Source	Particle size[a]	Optical properties[b]
S1	AuNR@SiO_2 (3 g/kg, EtOH)	University of Vigo	L: 62.6 ± 8.8 nm W: 14.4 ± 2.1 nm Shell 28.1 ± 3.0 nm	L_{max} 873 nm OD_{max} 132
S2	AgNT@PVA (1 g/L, H_2O, pH 4)	Nanocomposix	79.1 ± 34.7 nm	L_{max} 738 nm OD_{max} 140.0
S3	AgNT@ SiO_2 (1 g/L, H_2O, pH 8)	Nanocomposix	Core: 51.3 ± 26.4 nm Shell: 7.2 nm	L_{max} 828 nm OD_{max} 102.4
S4	AERODISP® W 7520 N (SiO_2, 10 g/kg, H_2O, pH 8)	Evonik®	135.1 ± 0.4 nm	n/a[c]

[a] Particle sizes are TEM-based as provided by the producer, except for entry S4 where data derive from dynamic light scattering.
[b] Optical properties derive from UV–VIS spectroscopy as provided by the producer: OD_{max}: maximum optical density (unitless); L_{max}: absorbance maximum in nm.
[c] SiO_2 is VIS-IR transparent.