



Analytical Methods

Feasibility of non-invasive detection of engineered nanoparticles in food mimicking matrices by Optical Coherence Tomography



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ABSTRACT

The study was dedicated towards the detection of Engineered Nanoparticles (ENPs) by means of Optical Coherence Tomography (OCT). Polymeric films were produced to mimic complex food matrices whereas gold nanorods (AuNRs) were embedded to act as ENPs. The straightforward coating application resulted in a sufficient film wetting, adhesion and homogenous AuNR distribution. Compared to food samples, these films are simpler and better defined. Such artefacts are therefore promising candidate materials for quality assurance and regulatory matters. The OCT investigations revealed a dependency of the measured signal intensity on the AuNR concentration in the film. The limit of detection for the setup and material was estimated to be -8 dB. This value corresponds to a ppm nanoparticle concentration being well below the concentration used in food additive applications. Thus, the findings indicate the potential of OCT to screen food/feed products for a number of ENPs.

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1. Introduction

Food contains natural nanomaterials in form of (assembled) structures of saccharides, fatty acids and/or amino acids like in the emulsion of milk which is seen harmful also with respect to particle size considerations.

This view on nanomaterials changes if it comes to artificially produced nanomaterials. Such engineered nanomaterials are used in food industry to enhance various product properties but are also applied in food packaging industry (Chaudhry, 2008; Sekhon, 2010). Thus, engineered nanomaterials are practically additives but can also be present in food as non-intended contaminants. A 'nanomaterial' as defined by EU is a 'material with any external dimensions in the nanoscale or having internal structure or surface structure in the nanoscale'. The term 'nanoscale' is defined as size range from approximately 1 nm to 100 nm. A nanomaterial as defined in the EU recommendation should consist for 50% or more of particles having a size between 1 nm and 100 nm. An engineered nanoparticle is a particle according to the above definition and is an intentionally produced material (EU 2011/696). The huge enthusiasm about the potential of nanomaterials also triggered safety concerns, partly caused by the often greater reactivity of nanomaterials: Nanomaterials have a large specific surface ($>150 \text{ m}^2/\text{g}$) causing an increased reactivity compared to bulk

materials. As a consequence EC released the Food Regulation (EU) 1169/2011 clarifying that food/feed manufactures will need to adjust product labels with respect to the presence of Engineered Nanoparticles (ENPs). To enforce the regulation, suitable detection methods need to be applied. However, these are not available at the moment (EFSA, 2009). On top of that, industry and regulatory bodies will demand fast and reliable methods for detection in various matrices. Therefore, non-invasive and non-destructive detection methods are very attractive from a commercial and practical point of view. The non-destructive manner gives mainly two advantages compared to methods requiring sample digestion. First, the specimen remains 'virgin' as before the test and can be reintegrated in the production line or used for further investigation. Second, the high speed of data generation is favourable if it comes to on-line applications. Regulation currently mainly applies to ingredients of food products, and does not specify concentration limits for nanomaterials. Therefore, no LOD/LOQ requirements are specified.

Optical Coherence Tomography (OCT), an interferometric imaging technique, is established in medical and material diagnosis (Shields, Materin, & Shields, 2005; Stifter, 2007; Zysk et al., 2007). Near Infrared (NIR) light having an optical power in the mW range is used to penetrate into a substrate. Structural information can be obtained from the optical interference (not to be mixed up with analytical interference as a source of bias in a measurement) of backscattered light with a reference light beam. Later, these information can be turned into 2D/3D images. OCT is regarded as safe

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and requires no special work protection. This is important when OCT is considered for outside lab applications like food production lines. OCT provides cross-sections of samples with a resolution better than 10 μm lateral as well as in depth. As OCT is sensitive to scattering and back reflecting structures, gold nanoparticles were reported to control the optical contrast in skin and mouse especially with tumour models (Kah et al., 2009; Kirillin et al., 2009). Further, Kah et al. investigated the OCT signal dependency on gold–silica nanoshell concentration in biological tissue mimics (Kah, Chow et al., 2009). This attracted attention with respect to OCT applications for screening purposes of food stuff (Grombe, 2011) as the obtained integral data deliver information on the presence of ENPs and their spatial distribution in a matrix. Such information is crucial with respect to the different ENP/foodstuff scenarios; intentional ENP addition or contamination with ENP. However, the reported study further concerns the quantitative nanoparticles detection.

Because the interpretation of data resulting from scattering material, such as complex foodstuff, is challenging, the use of model systems will be described. The model systems are beneficial because of (a) the known characteristics of the components and (b) the simple composition reducing material interactions which may lead to agglomeration of the nanomaterial and in turn may cause unwished and disturbing phase separation within the sample under investigation. The model system contains chemicals used in nano-colloidal chemistry to produce stable dispersions. Casting films of these dispersions is therefore more promising than using complex foods as dispersion medium. The approach uses polyvinylpyrrolidone (PVP) as matrix component and gold nanorods (AuNRs) as ENPs. PVP was chosen as it is used as food additive (E1201), it is a well-known stabilizing reagent for colloidal dispersions and it is a widely used chemical for thin film production. Because of the lack of ENP/food stuff materials for development of non-invasive detection techniques, the employment of well-characterised AuNR materials as ENP auxiliaries will be described. Two similar types of AuNRs were investigated because factors like source and preparation protocol influence material properties. A second AuNR therefore allowed to test the method for robustness against different batches/producers of the particles. In order to have materials as similar as possible AuNRs were chosen which carry polyethylene oxide chains immobilized to the particle surface leading to sterical stabilization of the colloidal dispersion. The observed similar physical characteristics guarantee the production of a subsequent series of data and the comparability of the results. The AuNRs have an optical activity in the Near Infrared (NIR) light range of 800–1000 nm being caused by the plasmon resonance of the AuNRs (Liz-Marzán, 2006). Therefore, OCT systems matching this spectral range are promising candidates for sensitive detection of AuNRs.

This initial study aims to investigate the appropriateness of OCT to quantitatively detect ENPs in model thin films. The latter are artefacts being more defined than complex ENP/food samples. Therefore, they are advantageous in calibration applications as well as in regulatory control and quality assurance.

2. Materials and methods

Characteristic data of both kinds of AuNRs dispersions used in this study are given in Table 1. They were purchased from Sigma Aldrich (#716871, Bornem, Belgium) and custom made by the University of Vigo, Spain, respectively.

The coating formulations containing AuNR species from A1 or A2 were prepared as follows.

The dispersion A1 was diluted with ultrapure water (MilliQ, 18 $\text{M}\Omega\text{ cm}^{-1}$) to 0.18 g/L and mixed with a 20 g/L aqueous polyvi-

Table 1

Gold nanorod (AuNR) dispersions for producing the coating formulations.

Entry	Dispersion	Source	Particle size ^a (nm)	Optical properties ^b
A1	AuNR (1.8 g/L, H ₂ O, pH 7.4)	Sigma Aldrich (#716871)	L: 41.0 $\pm$ 4.1 W: 10.0 $\pm$ 1.0	L_{max} 801 nm OD_{max} 60
A2	AuNR (7.2 g/L, 96% EtOH)	University of Vigo, Spain	L: 56.8 $\pm$ 5.0 W: 15.4 $\pm$ 1.0	L_{max} 848 nm OD_{max} 259

L, length; W, width.

^a Determined by TEM (provided by producer).

^b Determined by UV–Vis spectroscopy (produced by producer).

nylpyrrolidone (PVP K90, VWR International, Belgium) solution to give a Au-concentration of 4.5 mg/L. The resulting mixture was manually shaken until it became visually homogenous.

The dispersion A2 was diluted with an aqueous PVP solution (5 g/L) to reach Au concentrations of 20 mg/L, 2 mg/L, 0.2 mg/L and 0.02 mg/L. The resulting mixtures were manually shaken until they became visually homogenous.

2.1. Preparation of gold nanorod/polymer films

Microscopy slides (75 $\times$ 25 $\times$ 1 mm³) were cleaned with soap, rinsed with MilliQ water and ultrasonicated (50 W, 10 min) in ethanol. After drying, the slides were wetted with the respective coating solutions. A macroscopically homogenous film was produced using a K-hand coater (500 μm , R K Print Coat Instruments Ltd., UK). The wet coatings were placed in a fume hood for 18 h to evaporate the solvent at room temperature. The final specimens were put in sachets and air-tight sealed.

2.2. Optical Coherence Tomography

The principle OCT setup used in this project is based on a Michelson interferometer. Broadband NIR light is coupled into the Michelson interferometer and split into a reference beam, reflected at a mirror, and a sample beam. Light, which is back reflected or back scattered from the sample interferes with the returning reference light and is spectrally resolved. The measured interference spectrum is modulated with frequencies being proportional to the optical path length difference in the interferometer, and hence to the depth in the sample, where the back reflection occurs. Thus, the entire depth information (depth-scan) is encoded in one single interference spectrum and is accessible by applying a Fourier transformation. Entire cross-sections and three-dimensional stacks are acquired during lateral beam deflection across the sample.

The utilised OCT system is an in-house built spectral domain OCT system with a depth-scan rate of 11.9 kHz, where a spectrometer unit is used to gather the interference spectra. A superluminescence diode (SLD) with a centre wavelength at 880 nm and a total spectral width of 130 nm was used as a broadband light source resulting in a depth resolution (axial resolution) of 6.4 μm . The lateral resolution in the focus was 6.7 μm . The sensitivity was measured to be 102 dB. The light of the SLD was guided through a fibre-coupled setup via a fibre optic coupler to the scanner head, which contains the modified Michelson interferometer and two galvanometric scanners for beam deflection in both lateral dimensions. The optical power of the light incident onto the sample was below 2 mW. Details on the spectrometer design and scanner head of the OCT system have been published recently (Burkhardt, Walther, Cimalla, Mehner, & Koch, 2012; Meissner, Knels, Krueger, Koch, & Koch, 2009).

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