In-Situ STEM Analysis of Gold Nanoparticles to Understand Nu-cleation and Crystal Growth

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[Abstract:0544] OPY-023

Electroanalysis of pharmaceutical compounds

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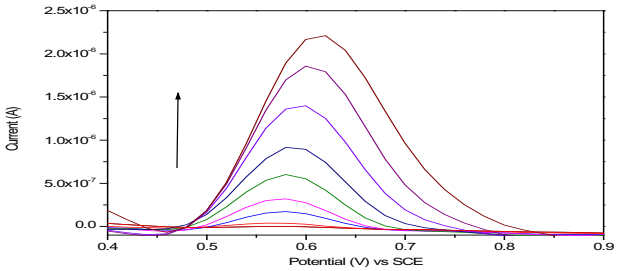
The Screen printed carbon electrode-CeO_2 approach shows many advantages over other electrochemical sensors reported in the literature; notably a simple fabrication process, the possibility of large scale-production, low-cost, portability, and the potential for use over wide concentration ranges of acetaminophen (ACOP), acetylsalicylic acid acid (ASA),caffeine (CAF) and diclofenac (DCF). Consequently, this method is worth consideration for both the individual and the simultaneous determination of all three molecules at trace levels in clinical and quality control laboratories. A LOD of 0.4 μmoL and sensitivity of 0.058 μA/μM were determined for DCF **(1).** The fabricated electrodes demonstrated superior reproducibility, with R.S.D of 2.7% even with a primitive casting of CeO_2 on the electrode surface.



(1)

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Keywords: CeO2, electroanalysis, screen-printed-electrode

[Abstract:0029] OPY-025

In-Situ STEM Analysis of Gold Nanoparticles to Understand Nucleation and Crystal Growth

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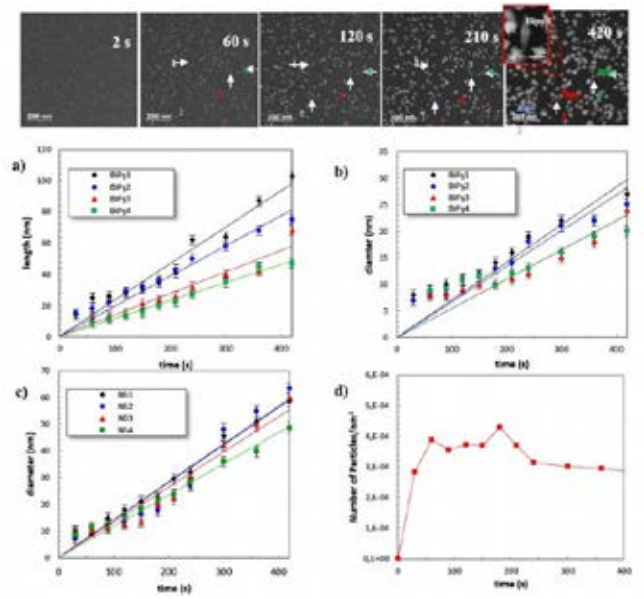
Liquid state transmission electron microscopy is a recent technique allowing researchers to visualize the nanoparticles directly in their liquid environment. Accurate visualization of growth in small nanoparticles is desired yet a challenging process due to limited resolution obtained due to surfactant present in the system. In this work, by using liquid environmental cell specimen holder (e-cell), developed for scanning transmission electron microscopy, we were able to monitor the formation of anisotropic gold nanoparticles from small precursors (< 7 nm) in surfactant assisted media, under electron beam. Technique offers the possibility to probe nanoparticles in-situ and to obtain detailed information on how nanoparticles grow in solution. However, under electron beam irradiation, due to radiolysis of water, some radicals are produced which can interact with the reactants and modify the chemical processes. Such phenomenon has to be considered during in-situ STEM analysis. In case of gold, this prior drawback can also be used to control the reaction. In our work, the incident electron beam was chosen to achieve two tasks simultaneously; first, as a radiation source to induce the radiolysis of water (which is responsible for the reduction of gold precursor) and the second, it allows the real time imaging of particles of interest in a thin layer of liquid. Initially, we have described influences of the beam parameters and the chemical conditions on the final shape of nanoparticles. Between these parameters, in case of altering the magnification (i.e. the dose rate), we have observed major differences in the shape of final nanoparticles obtained. Regarding to these differences, following formation mechanism has been proposed; at low dose rate, few number of produced seeds are able to grow into branched nanoparticles due to slow kinetics, caused simultaneously by slow ascorbic acid reduction at the surface of the nanoparticles and low number of radicals induced by electron beam, while at higher dose rate, the concentration of strong reducing agent is so high that the alimentation of the seeds will certainly proceed initially by fast feeding by pre-reduced Au(0) due to aqueous electrons and strong reducing agent and the slow feeding due to ascorbic acid reduction at the surface of the particles. Ad-

ditionally, the structure of final nanoparticles obtained by in-situ STEM and by gamma irradiation source (at similar chemical compositions) is compared to demonstrate the crucial importance of beam parameters on nanoparticle morphology.

Keywords: In-Situ STEM, crystal growth, gold nanoparticles

Figure 1



Above - Time resolved sequential images of Au NP growth at magnification 250k and pixel time 2 µS Below - Evolution of a) length b) diamater of four distiguished bipyramids c) diameter of four nanostars with time obtained at dose rate of 1.40 e-/sÅ2 d) Variation of the number of particles in unit area (nm2) with time

[Abstract:0102] OPY-026

Container-content interactions study in the cosmetic industry: chemical and toxicological approach

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Plastics are nowadays the principal materials used for cosmetic packagings. Indeed, they present many advantages such as low price, flexibility and resistance. However, these materials present a real environmental problematic. Moreover, due to their polymeric matrix, compounds such as additives (colorant, ink, plasticizers…) and non-intentionally added substances (also called NIAS) can migrate from the material into the cosmetic products. This phenomenon, called container-content interactions, is well studied in the industries of food, pharmaceutical products and medical devices. However, it is still unusual to see that kind of study on cosmetic products such as shampoo or lotion that are used daily. The possible carcinogenic, mutagenic or reprotoxic properties of the migrating molecules, called extractables and leachables, could potentially affect products' innocuousness, highlighting the importance of such study in the cosmetic area.

The aim of this work is to present a strategy of container-content interactions applied to cosmetic products. Combining material science, toxicology and analytical chemistry, a comprehensive analysis is used to screen a large spectrum of potential extractables and leachables for seven packaging materials (made up of polyethylene, polypropylene or styrene-acrylonitrile copolymer). The strategy developed is a multiple step strategy.

The first step, inspired from the European strategy for container-content interactions study in foodstuff, involves the use of simulants, *i.e.* simple matrices that mimic cosmetic products, for migration studies. Simulants proposed by the European food regulation were adapted to cosmetic products. In this way, seven simulants divided into two categories were identified: aqueous/ethanolic (Murat et al., 2019) simulants and viscous simulants (glycerin and liquid paraffin). They were put in contact with plastic packagings for one month at °50C. Twelve targeted compounds such as phthalates and plastic additives and twelve elements such as lead, arsenic and cadmium are qualified and quantified respectively using GC-QMS, LC-UV and ICP-MS according to a list of potential extractables and leachables pre-established by toxicologists. A screening study is also led by GC-TOF to identify potential unknown migrating compounds. For viscous simulants, different extraction METHODS: liquid-liquid extraction, liquid-liquid micro-extraction and solid phase micro-extraction were tested and compared in term of efficiency, environmental impact and practicality. All the results obtained were compared with toxicological thresholds set using reference values.

The second step is to study directly the packaging materials themselves. Extraction method prior to GC-MS/FID analysis was applied to packaging thanks to thermodesorption in order to analyze potential compounds leached directly from the source. A characterization of the materials was also made using thermal analysis such as differential scanning calorimetry to determine physico-chemical characteristics. These properties were helpful to explain the results obtained from simulants analyses.

Conclusions were made on the compatibility between a cosmetic product and a packaging material in order to ensure the safety of the consumers.

Murat, P., Ferret, P.-J., Coslédan, S. & Simon, V. Assessment of targeted non-intentionally added substances in cosmetics in contact with plastic packagings. Analytical and toxicological aspects. Food Chem. Toxicol. (2019). doi:10.1016/j.fct.2019.03.030

Keywords: Container-content interactions, cosmetics, phthalates