The silver nanowire based products fast development in a Safer by Design philosophy

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Fibrous particles interact with cells and organisms in complex ways that can lead to cellular dysfunction, cell death, inflammation and disease. Asbestos is present in all minds when a new nanofiber based products is being developped, not onmy with regards to its toxicity and deaths it has and is still responsinle for, but also to the economic burden due to the lack of recyclability of corrugated asbestos-cement sheets and building flocking. Now worldwide efforts are being made to develop conductive transparent networks (CTN) of metallic silver nanowires (AgNW) for portable touchscreen displays, active textiles, medical devices and paper printed electronics. These efforts raise the potential risk for intimate contact between novel fibers and human skin, and for the lack of recycling potential of these products.

In order to specifically evaluate the potential toxicity from dermal exposure, we investigated the dermal toxicity after acute exposure of polymer-coated AgNW with two sizes using two human primary keratinocyte skin cells. AgNW are rapidly and massively internalized inside cells leading to dose-dependent cytotoxicity that was not due to Ag^+ release, in contrast with most toxicity studies run with silver nanoparticles (AgNP). A combination of high-resolution coherent X-ray microscopy and fluorescence probes of cellular response show that AgNW fate and cellular toxicity is determined by the interplay of the membrane forces generated during endocytosis, the stiffness of the AgNW and the strength of the plasma membrane. Although 30- and 90-nm AgNW are readily internalized, the thinner NW are mechanically crumpled by the forces of endocytosis while the thicker nanowires puncture the enclosing membrane, release silver ions to the cytoplasm and initiate oxidative stress.

The nanosafety community has sought ways to design nanomaterials to lessen innate toxicity. However, there are few practical examples because we frequently lack clear guidelines for toxicity and because of competition between nanosafety and technical performance targets. Here we conclude from our toxicity study that a material property, namely nanowire stiffness as controlled by diameter, controls the cytotoxicity of AgNW to human non-immune cells without deterioration of critical CTN performance parameters, resistivity and haze. This finding extends the fiber pathology paradigm and will enable the manufacture of safer-by-design large scale nanowire consumer products.

The safer-by-design concept further requires the nanomaterial-based products to be engineered in a such way they can be recycled. If the case of paper-printed electronics, their potential use in every day products such as food packaging, phone touch screens, or solar pannels requires the recycling of such special papers to be insured and to follow the process of reglar paper recycling. We will be discussed the implied characteristics, namely the non toxicity of the product (the recycled paper), the lack of significant amount of silver in the recycling plant waste waters, and ideally a close loop for silver as well.

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Toxicity evaluation of platinum nanoparticles on proteins using Synchrotron Radiation Circular Dichroism

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The efficiency of platinum [1, 2] based nanoparticles to amplify the effects of radiation therapy at molecular level and cellular level has been proved by our group. Nanoparticles (NPs) can be administrated by intratumoural or intravenous injection. Considering the side effects (injection site pain and erythema, and pyrexia) of the former case, intravenous injection is favorable. When Pt NPs enter the bloodstream, they could rapidly interact with proteins. Unexpected interaction between Pt NPs and proteins might lead to toxicity. Therefore, it's important to understand the effects of Pt NPs on blood proteins such as Human Serum Albumin (HSA).

The Synchrotron Radiation Circular Dichroism (SRCD) is a very powerful and sensitive technique to elucidate the conformation of proteins. We used the far-UV SRCD spectra to explore the secondary structural changes of HSA in the presence of Pt NPs at different concentration at 37°C. The thermal stability of HSA in the presence of Pt NPs was assessed by analyzing changes in the SRCD spectra with increasing temperature 26~95°C.

No significant changes of the secondary structure of HSA have been observed. Denature temperature of HSA showed a single exponential growth as a function of increasing ratio of Pt NPs/HSA. We assume Pt NPs can stabilize human serum albumin when exposed to UV radiation.

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Reactor-injector of nanoparticles coupled with plasma processes

A safer method for the deposition of nanocomposite thin films

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Abstract (No longer than 250 words, Calibri 12, single line spacing, black)

Nanocomposite thin films (e.g. thin films with nanoparticles embedded in a matrix) receive a great interest as they develop multi-functional properties - the concentration, size, shape and distribution of nanoparticles together with the characteristics of the matrix contributing to the overall properties.

A lot of plasma processes are under development in such field. The simplest method is based on the injection of suspensions of ex-situ preformed nanoparticles with the matrix precursor(s) in the plasma reactor. However, this method introduces environmental and safety risks related to nanoparticles handling. Hence, even if nanocomposite materials exhibit attractive multifunctional properties, one needs to develop controllable, sustainable and as green as possible methods to process them.

Herein, we report the development of a direct liquid reactor-injector (DLRI). This method allows (1) to synthesize well-controlled nanoparticles directly in the device from liquid precursors and (2) to spray them in a pulsed regime in the final low-pressure plasma process without any handling. As a proof of concept, nanocomposite thin films consisting in isolated 6 nm in diameter crystalline ZnO nanoparticles dispersed in different matrices are reported.

Far to be limited to low-pressure plasma processes, DLRI is compatible with various wet or dry processes. Hence, DLRI offers a safe way for the preparation of multifunctional nanocomposite materials that should definitely impact nanotechnologies.

Session: Nanotoxicity & Safer by Design in collaboration with LabEx SERENADE
Keywords: engineered nanomaterials, sludge, biosolids, wastewater, environment.

Impact of a cocktail of nanomaterials on the operation of wastewater treatment plant and the valorization of biosolids

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More than 1800 Engineered Nanomaterial (ENM)-enabled products are currently on the market[1]. The ENMs released will go down the drain to wastewater treatment plants (WWTPs). After water treatment, the residual sludge is valorized in digesters for biogas production and in agriculture, with land application of the biosolids. NanoSTEP program[2] addresses the behavior, fate and impacts of ENMs on the WWT operation and the energy recovery from biosolids through an interdisciplinary approach.

The ENMs were processed to mimic their lifecycle (combusted CeO_2-based diesel additive[3], sulfidized nanoAg, and two nanoTiO_2 used as photocatalyst and UV absorbant). ENMs were chronically added to an aerobic bioreactor supplied by wastewater. Sludge from the process then fed an anaerobic digester. The EMNs concentrations fitted the predicted environmental concentrations in WWTPs[4]. We monitored the operation parameters, wastewater treatment efficiency, microbial enzymatic activities and communities, and biogas production. We analyzed the partitioning of ENMs between the water and solid phases and the speciation of Ce and Ag in the biosolids.

[1] http://www.nanotechproject.org/cpi/

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Keywords: Titanium dioxide, Paint, photocatalysis, Safer by design

SafeTiPaint: Toward a safer by design approach of photocatalytic paint to improve air quality

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Air pollution is becoming an increasingly concern for public health. WHO reports that it causes 8 million of premature deaths every year worldwide. One promising way of remediation of this pollution could come from photocatalytic processes, which aims at converting gaseous pollutants, such as Volatile Organic Compounds into CO_2.

The main objective of the SafeTiPaint project (part of the LabEx SERENADE), is to design a photocatalytic paint with a safer by design approach, meaning to consider all the aspect of the product lifecycle from the material conception to the end of life of the product. The tasks were divided into different laboratory partners with specific expertise such as synthesis, paint formulation, air quality, toxicology. Different types of photocatalyst of Titanium Dioxide (TiO_2) with a coating were synthesized, and their photocatalytic activities were tested in the laboratory. Among them, the best candidates were selected and incorporated into 7 new paints and applied on standard Leneta substrate. One aspect of the safer by design is to prevent particle release by testing the mechanical durability over time when exposed to various climatic conditions. Photocatalytic efficiency of the paint was also investigated. To do so, paints were (i) placed in an ageing climatic chamber with controlled parameters (light, temperature, relative humidity …) over 500 and 1000 hours, (ii) photodegradation efficiency was tested for brand new and aged paints, (iii) mechanical abrasion was performed with aerosols emission measurements. This presentation will give a brief overview of the project with a focus on the main results.

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Keywords: nano-titanium dioxide, sunscreen, environmental fate, ecotoxicity, risk assessment

Implications for sunscreen eco-design: Fate and toxicity of nanoparticulate TiO_2 UV-filters throughout sunscreen life-cycle

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Evaluating the impacts of sunscreens on both human and environmental health remains an important challenge as widespread use continues and new formulations are developed. Titanium dioxide (TiO_2) nanoparticle UV-filters may offer a safer alternative to organic filters, however their fate and impact are not fully understood and regulation regarding risk is still under consideration. After leaving the skin either through swimming or everyday use and subsequent washing, TiO_2 nanomaterials contained in sunscreens can be released into rivers, lakes, sea shores, and/or sewage treatment plants. Furthermore, disposal of sunscreen containers in solid waste can result in TiO_2 nanomaterial release into landfill leachate.

The present work aims to develop the eco-design of sunscreens through the minimisation of risks associated with nanomaterials incorporated into the formulation by reducing their potential release and/or toxicity. Consequently, every stage of the sunscreen life-cycle must be considered, from manufacturing and consumer use to end-of-life and impact on the exposed environment. The risk to the direct aquatic environment (e.g., fresh water, sea water) was assessed by evaluating the release and degradation of relevant nano-TiO_2 UV-blockers of varied surface coating (e.g., stearic acid, polydimethylsiloxane, and silica) through a simulated laboratory aging procedure. Ecotoxicity of these by-products was evaluated on coral symbiotes and sea urchins. Finally, end-of-life was considered by determining TiO_2 nanomaterial release from sunscreen and stability in the presence of fresh and mature landfill leachates.

These insights will help guide regulations, provide better information for consumers, and assist manufacturers in incorporating an eco-design approach in consumer product development.