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Chitosan Nanoparticles as Stabilizer of Hydrogen Peroxide Based Disinfectants

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The development of new disinfectants is a laborious and challenging task that involves selecting ingredients and conducting many trials to evaluate the performance of formulations. Among the disinfectants currently found on the market, products that use hydrogen peroxide as a base stand out for their high oxidizing power and for being more environmentally friendly compared to other formulations. The main drawback of using hydrogen peroxide based disinfectants is the high instability of this compound, which rapidly degrades in the presence of heat and light. Thus, inorganic and organic stabilizers are commonly added to formulations to increase the stability of the final product. However, many of these compounds are considered harmful to the environment, prompting the search for environmentally sustainable stabilizers.

The Biochemical Engineering Laboratory at Western University, supervised by Professor Lars Rehmann, has a project in partnership with the Germiphene Corporation that produces disinfectants. The main objective of the partnership is to develop and apply rapid methodologies for screening different disinfectant types. Among the products being developed by the company, we highlight the hydrogen peroxide-based disinfectant using chitosan nanoparticles as a stabilizer. The goal is to obtain a product that is both effective and environmentally sustainable.

Chitosan is the second most abundant natural polymer in the world, obtained by deacetylation of crustacean exoskeleton chitin. Chitosan is superior to other stabilizers found in the market, because besides the controllable mechanical properties, it is a non-toxic, biodegradable and biocompatible compound. The research is in the stage of chitosan nanoparticles production. In this step, the Scanning Electron Microscope (SEM) at the Western Nanofabrication Facility has assisted in the image capture to evaluate the size and shape of nanoparticles. In the Figures 1a and 2a it is possible to observe some images captured through SEM of chitosan nanoparticles produced from different methods.

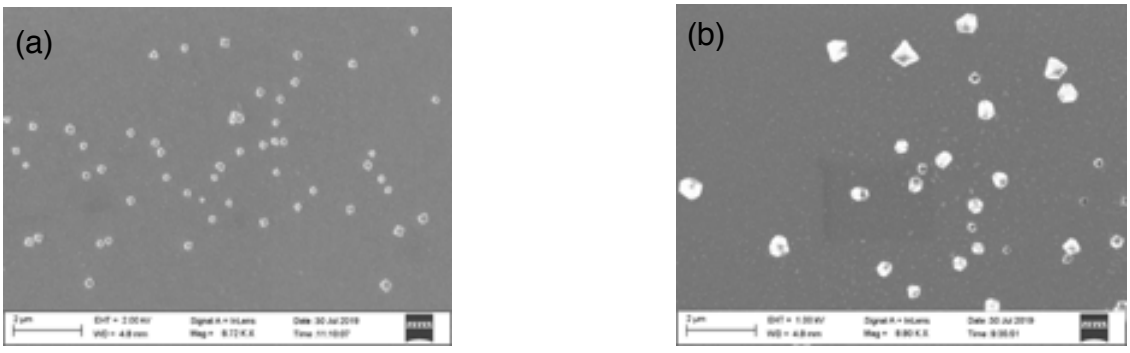

***Figure 1 (a) and (b)**: Chitosan nanoparticle images captured through SEM at the Western Nanofabrication Facility*

Plasmonic and Nonlinear Optical Properties of Gold Metastructures

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Plasmonically activated optical processes at the surface of nanostructures have shown an increase in usage for applications ranging from bio-imaging, optical sensing and filtering, surface chemistry, and more. Of interest are plasmon enhanced nonlinear optical (NLO) effects due to their quadratic dependence of the impinging electromagnetic field. In second-order NLO effects the process will vary with E^4, where E is the electric field of the input light. By using advanced lithographic techniques with a spatial resolution down to 10 nm, nanostructures can be produced and tailored to have specific optical properties ranging from the UV to the THz range.

An interesting series of structures are metastructures with self-replicating features known are dendritic fractals, or dendrimers. These dendrimers have already been exploited for surface-enhanced spectroscopies.[1] These plasmonic properties make them good candidates for a second-order nonlinear optical process known as second-harmonic generation (SHG). This process relies on a material absorbing two photons at a frequency ω and emitting one at 2ω. Due to its second-order nature, SHG has selection rules based on the symmetry of the material, meaning it can not contain a center of inversion. The dendrimers present a prime candidate to probe this nonlinear optical process due to the high control over the symmetry, dimensions and optical properties.

One facet of my PhD, is the development, production, characterization, and optimization of nanostructures that are designed to exhibit large SHG activity. Using electromagnetic calculations, the design and tuning of these dendrimers can be reliably predicted even before production. These dendrimers can then be fabricated using the electron beam lithography available at the Western Nanofabrication Facility. Once produced, the structures are optically characterized using a variety of techniques (extinction, SEM, ellipsometry) and then tested for SHG activity using an SHG microscope that we have developed. Nanostructures containing a plasmonic resonance at either the fundamental or second-harmonic wavelength will show an enhanced SHG activity. Furthermore, the symmetry of the structures can be controlled by modifying the number of arms of the dendrimer, ranging from C_3 to C_5 symmetries. By outwardly adding more generations to the dendrimers, more interesting plasmonic properties start to show themselves, adding to their potential as SHG-active candidates.

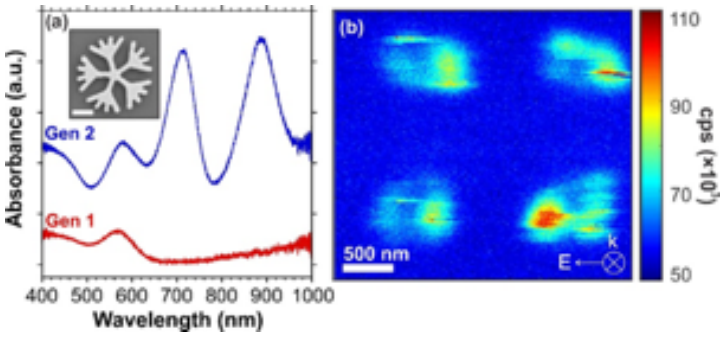

Figure 1. (a) Absorption measurements of a five-branched dendrimer for generations 1 and 2 (generation 2 in the inset, scale bar is 200 nm). The SHG activity for a five-branched generation 2 is shown in **(b)**.

1. Wallace, G. Q.; Lagugné-Labarthet, F., Advancements in fractal plasmonics: structures, optical properties, and applications. *Analyst* **2019**.

Using Photomasks to Fabricate Multi-Electrode Arrays For Corrosion Studies

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Corrosion involves two coupled half-reactions, an anodic half-reaction in which metal is oxidized, and a cathodic half-reaction in which the electrons released in the anodic half-reaction are consumed in reducing an oxidant species. When the two half-reactions occur at different locations, we see localized corrosion (e.g., pitting or crevice corrosion) at the location of the anodic half-reaction. In cases of uniform corrosion, where the metal surface is attacked relatively evenly at all exposed locations, we are uncertain about the locations of the anodic and cathodic half-reactions relative to each other. It could be that both half-reactions take place simultaneously at the same site or that the cathodic and anodic locations are interspersed at the atomic level such that distinguishing them is impossible. A third option, which many corrosion scientists think feasible, is that there are separate anodic and cathodic sites on a surface undergoing uniform corrosion, but they move about the surface over time, such that the net result is a nearly equal amount of metal oxidation at every location on the surface.

To investigate the latter hypothesis we use an array of microelectrodes containing 50 closely spaced electrodes in a rectangular pattern. On a macro-sized electrode undergoing uniform corrosion, no electrical current flow is seen, because all electrons produced by metal oxidation would be consumed by oxidant reduction on the same surface, leaving none to flow through a measuring device; however, a microelectrode may be small enough that its entire surface can be occupied by a single anodic or cathodic event, in which case, for an array closely spaced microelectrodes, the electrons would have to flow through an instruments ammeters to travel from anodic to cathodic electrodes.

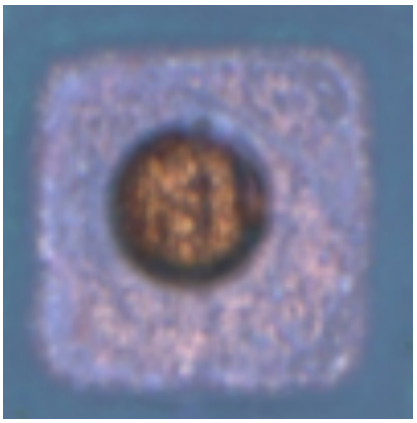

Figure 1. *An optical image of a single electrode in an array.*

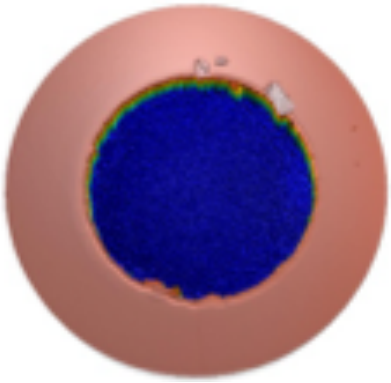

Figure 2. A *3d reconstruction of the electrode.*

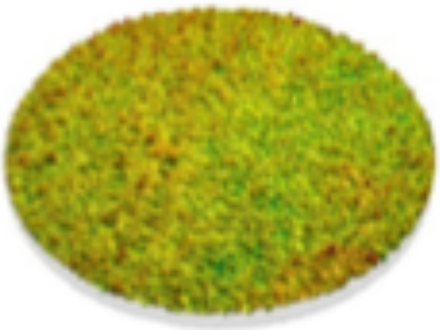

Figure 3. *A 3d reconstruction of the inner portion of the electrode.*

An array of microelectrodes that is able to probe the cathodic and anodic activities at individual sites requires a couple key criteria. First, the microelectrodes must be uniform in shape, size and spacing. Second, to properly investigate individual anodes and cathodes the array must be easily fabricated and easily modified. With these criteria fulfilled arrays with varying electrode shapes, sizing, spacing and order can be made.

At the Western Nanofabrication Facility, a fairly quick process of cleaning, spin coating and using a photomask with UV curing is done to create these arrays containing 50 circular 50 µm diameter electrodes in a 5x10 rectangle. To avoid non-uniformity from handmade/casted electrodes, printed circuit boards (PCBs) are used as the starting substrate (pre-patterned electrodes and spacing) which are masked using the polymer SU8-3000 and then selectively exposed to open up holes in the polymer that fit the electrode parameters. Spin coating is often done on extremely flat substrates, however spinning a coating onto a non-uniform substrate such as a circuit board is a relatively unexplored concept. In order to do this correctly it requires optimization of various parameters such as: bake times, cure time, spin times, spin speed, developing times and addition of a thinning agent. The process is still undergoing optimization, but it is possible to create repeatable and uniform arrays of desired size and spacing.

The arrays are characterized using laser confocal microscopy which allows for 3D reconstruction of each electrode that also shows the relative uniformity of each pad. By mildly corroding these

ISO 25178	
Height Parameters	
Sq	11 um
Ssk	-0.61
Sku	1.4
Sp	13 um
Sv	17um
Sz	30 um
Sa	11 um

Figure 4. *The associated height parameters of the 3d reconstruction of the inner portion of the electrode.*

electrodes we can obtain reconstructions from before and after with height and roughness parameters that dictate how much damage is done on each electrode which can then be related to the measured current. All Figures show a sample of a single exposed electrode, as well as the analysis done, including the typical parameters for the electrodes all of which are highly repeatable.

This is a novel approach and an underexplored topic in corrosion science, which can help analyze fundamental processes. With further testing and optimization, there is also an opportunity to fabricate more complicated arrays which include tiny sensor electrodes (for pH, [Cl^-], and local potential) that could be used to obtain real-time, localized chemical data from buried interfaces, or inside corroding cracks and crevices.

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