In-Situ Monitoring and Nanoscale Structure Characterization of Electrodeposited Chitosan Films

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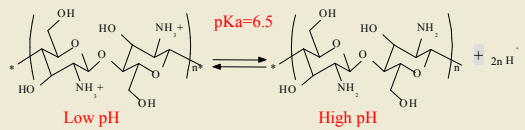
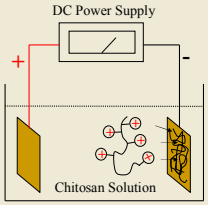
Unique Properties of Chitosan

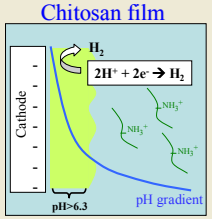
- Amine rich polysaccharide
- Able to anchor biomolecules
- pH dependent solubility



Electrodeposition of Chitosan



Localized high pH region generated electrochemically due to hydrogen evolution. Chitosan molecules deprotonate and immobilize at electrode surface. Electrochemical reaction rate depends on current density.



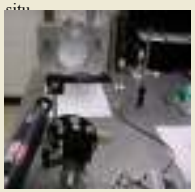
Motivation

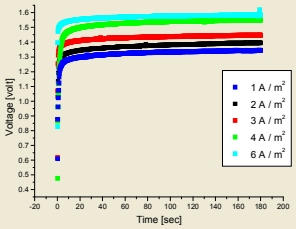
Chitosan has served as a robust and reproducible scaffold for biomolecule assembly by electrodeposition at specific sites on microfabricated devices. However, its growth and properties are not well understood as a function of deposition parameters. To better understand the materials and process science of electrodeposition on gold electrodes, in-situ characterization techniques and post-deposition measurements of air-dried films were performed

Characterization Methods

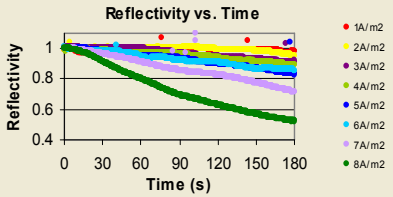
In-situ

Deposition cell is equipped to take electrical, optical, and pH data in-situ



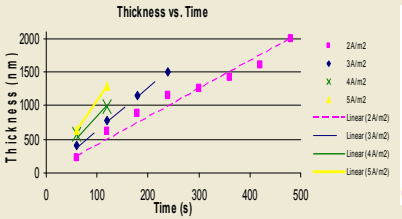


Voltage data taken simultaneously has greater sensitivity at the start of the deposition while the reflectivity is more sensitive at the end



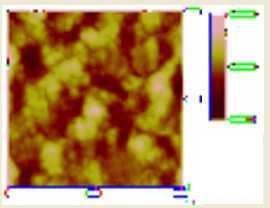
Reflectivity is inversely proportional to the thickness of the film. Growth rate increases with current density.

Post-Deposition



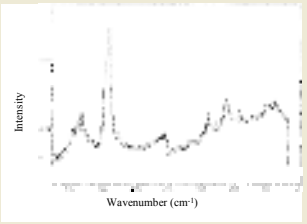
Profilometry is used to measure the average physical thickness of the chitosan layer across an electrode. The slope of the graph, the growth rate, increases with current density. For each unit increase in A/m^2, the growth rate increases by about 2.2 nm/s.

A/m2	Slope (nm/s)
2	4.15
3	6.33
4	8.46
5	10.8

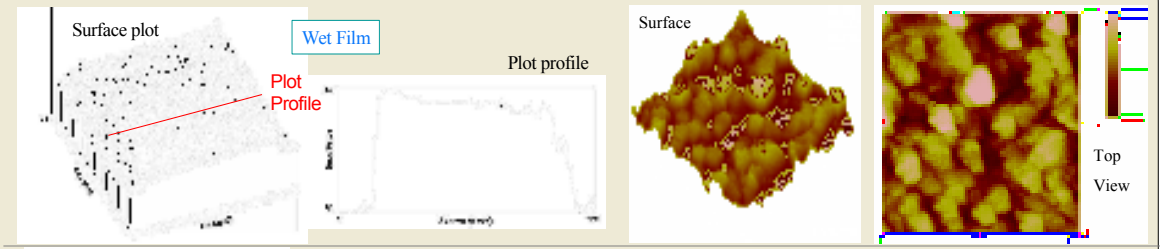


A typical **AFM** height image of a chitosan surface shows ridges and trenches made of spherical nanostructures.

Vibrating functional groups cause **Raman** scattering, producing peaks at certain wavenumbers specific to chitosan.



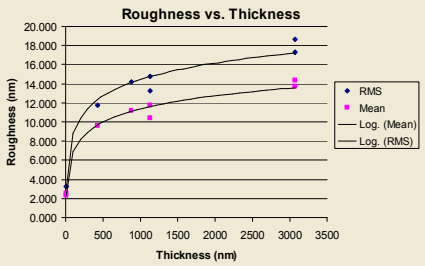
Collapse of Film Structure During Drying Roughens Surface Unpredictably



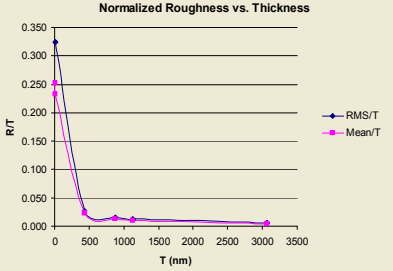
In-vitro (wet) fluorescence images show fairly smooth distribution of chitosan, whereas dried films were much rougher, indicating non-uniform collapse of structure during drying.

AFM images of dried films depict variable, rough morphology not directly correlated to deposition conditions. Hydration increases surface smoothness and homogeneity. AFM images show that wet films have circular, relatively smooth plateaus as compared with the jagged ridges and trenches formed when the films are dried.

Dried Film Roughness vs. Thickness Supports Growth by Nucleation



Roughness increases logarithmically with thickness.



The relative roughness decreases with increasing thickness.

Data support nucleation or "run away" type growth. We theorize that the first chitosan molecules are attracted to charge concentrations i.e. bumps in the gold electrode. Subsequent molecules prefer to attach to the growing mound of chitosan causing the roughness to increase very quickly in the beginning. As time progresses, the radius of curvature and thus charge concentration decreases, decreasing the driving force for nucleated growth. Lateral growth causes mounds to grow into each other and the roughness to slow and level off.

Conclusions and Future Work

Various properties of dry films are not reproducible with identical deposition conditions. Dry morphology does not accurately reflect the structure of wet films. Nucleation type growth is proposed from roughness vs. thickness data.

In the future we hope to study further the properties of hydrated films in order to fully understand chitosan as a platform for biotechnology applications.

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