BIOPOLYMER-PATTERNED NANOPARTICLE DEPOSITION

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[5]Environmental Sciences Division: Oak Ridge National Laboratory

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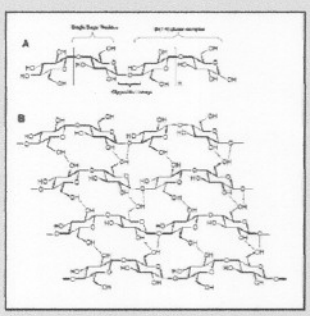
Abstract

Bacterial cellulose consists of a hydrophilic biopolymer network that provides a suitable matrix for the nucleation and deposition of a number of minerals and metals that are of interest for technological applications. Incubating the cellulose in aqueous salt solutions permits the homogenous deposition of ceramic particles such as calcium-deficient hydroxyapatite and calcium carbonate. Catalytic metals, such as palladium and silver, can be incorporated into the polymer backbone by a redox reaction catalyzed by the reducing ends of the cellulose. Platinum can also be incorporated into the cellulose by infusing hydrogen as a reductant. Bacterial culture conditions modulate the size, shape, porosity, and thickness of the cellulose matrix used for biopatterned deposition. The size and composition of metal and ceramic particles formed within the cellulose matrix can be readily determined by tunneling electron microscopy (TEM), laser-induced breakdown spectroscopy (LIBS), and x-ray diffraction (XRD).

Bacterial Cellulose

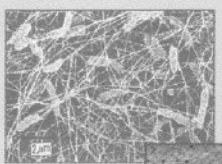
Plants produce most cellulose, but certain bacterial species secrete pure cellulose as small fibers in a hydrogel network



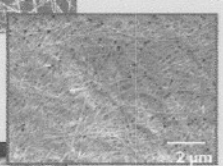
Cellulose consists of β-(1,4) glucan sugars

Extensive hydrogen bonding between chains and fibrils gives cellulose high strength

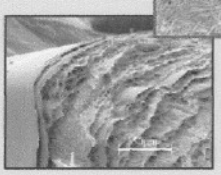
Hydroxyl groups enable chemical modifications



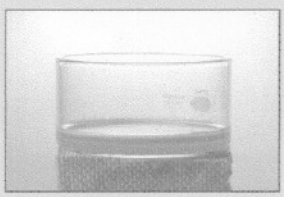
Bacteria extruding cellulose fibers (Klemm et. al, *Prog. Polym. Sci* 26, 2002)



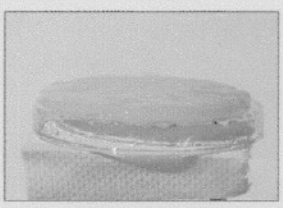
Cellulose fibers twist and overlap to form parallel crystal lattice plane



Planes stack on top of each other to form the thickness of the "pellicle"



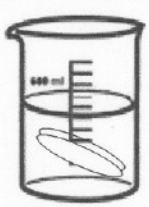
Bacterial Cellulose is synthesized by the *Gluconacetobacter hansenii* bacteria in Schramm-Hestrin media.



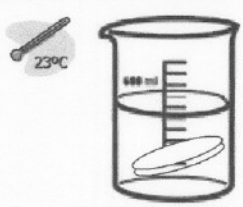
Cellulose pellicle is purified by treatment with 90°C water and 1% NaOH

Deposition of Ceramic Particles

After incubation in aqueous salt solution, trapped ions in the cellulose matrix precipitates minerals

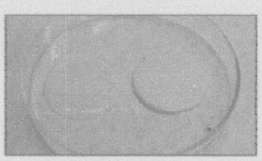


Cellulose is incubated in 100mM $CaCl_2$ for one day

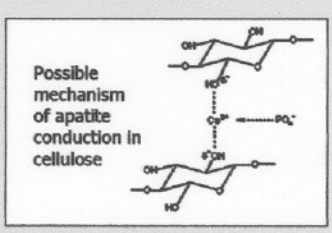


For Calcium-Deficient Hydroxyapatite, cellulose is then incubated in Sodium Phosphate Dibasic solution for one day

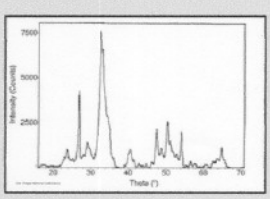
For Calcium Carbonate production, cellulose is incubated in Sodium Carbonate solution for one day (instead of Na_2HPO_4) following $CaCl_2$ incubation



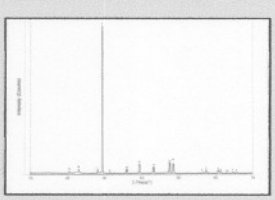
Left: Unaltered Bacterial Cellulose
Right: BC after incubation in 100mM $CaCl_2$ and 60mM Na_2HPO_4



Possible mechanism of apatite conduction in cellulose



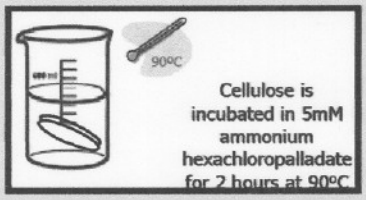
Peak at 23° 2θ characteristic of cellulose, remaining peaks characteristic of calcium-deficient hydroxyapatite



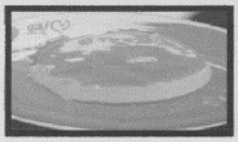
Peak at 23° 2θ characteristic of cellulose, remaining peaks characteristic of calcium carbonate

Palladium Bacterial Cellulose

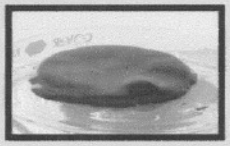
Palladium deposition is catalyzed by the reducing ends of the cellulose chains



Cellulose is incubated in 5mM ammonium hexachloropalladate for 2 hours at 90°C



Native Bacterial Cellulose

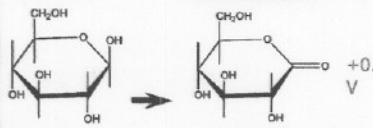


Palladium Bacterial Cellulose

Reduction of $(NH_4)_2PdCl_6$ to Palladium by Glucose

Oxidation - Reduction Potential

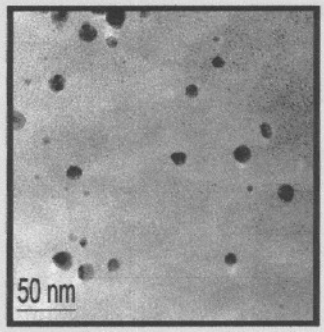
β-D Glucose → Gluconolactone +0.45 V



$+ PdCl_6^{2-} + 4e^-$ $+ Pd + 6Cl^- + 2H^+$

$PdCl_6^{2-} + 2e^- \rightarrow PdCl_4^{2-} + 2Cl^-$ +1.29V

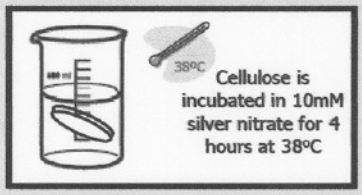
$PdCl_4^{2-} + 2e^- \rightarrow Pd\downarrow + 4Cl^-$ +0.62V



TEM Image of Palladium Particles in Bacterial Cellulose

Silver Bacterial Cellulose

Silver deposition is catalyzed by the reducing ends of the cellulose chains



Cellulose is incubated in 10mM silver nitrate for 4 hours at 38°C

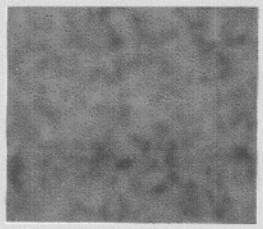
Reduction of $AgNO_3$ to Silver Reduction Potential

Oxidation- by Glucose

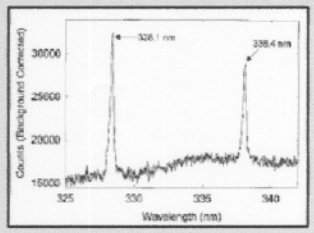
$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H^+ + 2e^-$ +0.45V

$Ag^+ + e^- \rightarrow Ag\downarrow$ +0.80V

Dried Native Bacterial Cellulose: 150X Magnification



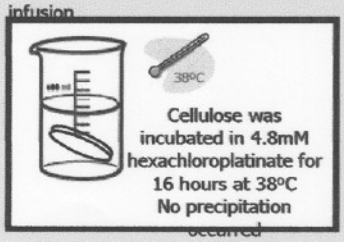
Dried Bacterial Cellulose after Incubation in 10mM $AgNO_3$: 150X Magnification



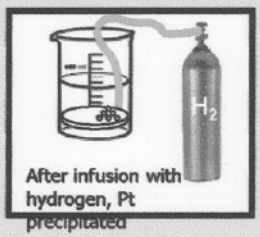
Laser-Induced Breakdown Spectra of Silver-Doped Bacterial Cellulose (from Martin et. al *Applied Optics* 42, 2003)

Platinum Bacterial Cellulose

Platinum deposition was not observed by catalysis with cellulose reducing ends, but did occur with hydrogen infusion



Cellulose was incubated in 4.8mM hexachloroplatinate for 16 hours at 38°C No precipitation occurred

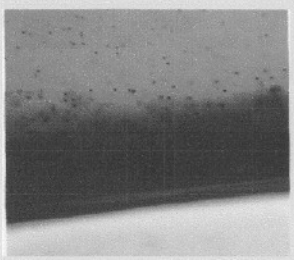


After infusion with hydrogen, Pt precipitated

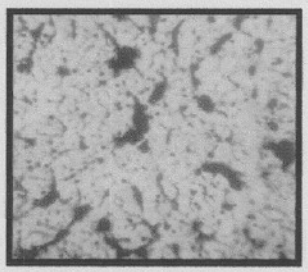
Reduction of Na_2PtCl_6 to Hydrogen

Oxidation- Platinum by Potential

$PtCl_6^{2-} + H_2 \rightarrow Pt\downarrow + 6Cl^- + 2H^+$ +0.73V



Platinum Deposition in Bacterial Cellulose Catalyzed by Hydrogen Infusion: 150X Magnification



Distribution of Platinum Particles in Bacterial Cellulose after Hydrogen Infusion: 150X Magnification

Applications for Cellulose Composites

- Hydroxyapatite bacterial cellulose may find use as an orthopedic biomaterial, as a form of stabilized hydroxyapatite material for absorption of proteins, or for the removal of water or soil contaminants such as Pb, Cd, Zn, U, and Sr
- Palladium and Platinum metals can absorb large volumes of hydrogen making these metals suitable for hydrogen storage.
- Palladium metal immobilized in cellulose can catalyze hydrogen oxidation and oxygen reduction making this composite suitable as the catalyst layer in a membrane electrode assembly for poly electrolyte membrane class fuel cells
- Photoactive silver nanoparticles have been investigated for optical data storage applications and for use in biological labels and electroluminescent displays
- The cellulose "template" can be modified into different shapes, sizes, and porosities to vary the size of the metal/ceramic particulates
- Bacterial cellulose can be easily dried down to a paper-thin membrane or

Acknowledgments

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- Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725
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