Increasing environmental pollution, global climate change and petroleum resource depletion are important indicators for the inevitable replacement of fossil-based polymer materials with more sustainable counterparts. Hence, the development of bio-based materials from renewable resources, such as cellulose, is of great importance. Thus, herein, we introduce a rapid and homogenous microwave assisted synthesis of high molecular weight (59 kDa ≤ M_n ≤ 116 kDa) short chain (mixed) cellulose esters (CEs) with variable acyl side chain length (2 < C < 8) and adjustable degree of substitution (DS) (1.99 ≤ DS ≤ 2.34) by using a TMG/CO_2 switchable solvent system. Accordingly, (mixed) CEs were synthesized by implementing tetramethylguanidine (TMG) into a switchable solvent system (TMG/CO_2/DMSO) and simple variation of reaction parameters, followed
by in-depth structural characterization via IR, $^1$H NMR, $^{13}$C NMR and SEC. Examination of the structure-property relationships revealed a decrease in glass transition temperature ($177^\circ \text{C} \leq T_g \leq 204^\circ \text{C}$), an increase in surface hydrophobicity, i.e. water contact angle (WCA) ($65^\circ \leq \text{WCA} \leq 98^\circ$) and a thermal stability, i.e., $T_{d,5\%}$, up to $333^\circ \text{C}$.

CELL 3904156

Sustainable procedures for cellulose derivatizations using the DMSO/DBU/CO$_2$ switchable solvent system

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Cellulose derivatives with tunable material properties are promising biobased alternatives to existing petroleum-derived polymeric materials. However, the chemical modification of cellulose is very challenging, often requiring harsh conditions, reagents in over-stoichiometric amounts, and complex solubilization or activation steps. We demonstrate a more sustainable synthesis approach for cellulose acetate using the DMSO/DBU/CO$_2$ switchable solvent system under mild reaction conditions, showing high conversions. Vinyl acetate, as a more benign acetylation agent, was used and high recycling ratios of all employed components were demonstrated. Less cellulose backbone degradation compared to the commercially mainly used Acetic Acid Process was confirmed via SEC, resulting in improved mechanical properties. Furthermore, a direct synthesis of cellulose acetates with lower degrees of substitution (1.0–2.5) could be demonstrated. In heterogeneous approaches, peracetylation with subsequent partial hydrolysis is necessary to obtain cellulose acetates with lower degrees of substitution (< 3.0).

In another approach, the same solvent system was used to combine tandem catalysis with cellulose derivatization in a one-pot procedure. Cellulose was solubilized and subsequently functionalized with isothiocyanates, which were formed in situ via a catalytic
sulfurization of isocyanides with elemental sulfur. The only necessary catalyst in this system is the organobase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which was proven to promote all three transformations. This process prevents the exposure and handling of reactive isothiocyanates for the synthesis of O-cellulose thiocarbamates and was demonstrated to be beneficial in terms of sustainability and efficiency compared to a stepwise synthesis.

Figure caption: Schematic representation of the one-pot cellulose dissolution and derivatization via a tandem reaction approach forming O-cellulose thiocarbamates.

CELL 3921214

Synthesis of multi-reducing end polysaccharides and its derived hydrogels

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Site-specific modification is a great challenge for polysaccharide scientists. Chemo- and regioselective modification of polysaccharide chains can provide many useful natural-based materials and help us illuminate fundamental structure-property relationships of polysaccharide derivatives. The hemiacetal reducing end of a polysaccharide is in equilibrium with its ring-opened aldehyde form, making it the most uniquely reactive site on the polysaccharide molecule, ideal for regioselective decoration such as imine formation. However, all-natural polysaccharides, whether they are branched or not, have only one reducing end per chain, which means that only one aldehyde-reactive substituent can be added. We introduce a new approach to selective functionalization of polysaccharides as an entrée to useful materials, appending multiple reducing ends to each polysaccharide molecule. Herein we reduce the approach to practice using amide formation. Amine
groups on monosaccharides such as glucosamine or galactosamine can react with carboxyl groups of polysaccharides, whether natural uronic acids like alginates, or derivatives with carboxyl-containing substituents such as carboxymethyl cellulose (CMC) or carboxymethyl dextran (CMD). Amide formation is assisted using the coupling agent 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM). By linking the C2 amines of monosaccharides to polysaccharides in this way, a new class of polysaccharide derivatives possessing many reducing ends can be obtained. We refer to this class of derivatives as multi-reducing end polysaccharides (MREPs). The application of the multi-reducing end polysaccharides has been demonstrated by making hydrogels using multi-reducing end alginate with polyethyleneimine (PEI). The two polymer solutions can form a gel at room temperature after 24 hours. Acetic acid can be added to accelerate the gelation process, which 5 ul acetic acid can induce fast gelation within seconds.
CELL 3905883

Bending mechanism of agarose scaffold composites

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In the field of biomaterial design, materials that can be actuated by external stimuli are of particular interest in the production of smart materials. Controlling a material's shape through external stimuli such as humidity allows objects to have additional functionality and imparts new methods of control. Agarose is one such biomaterial that is non-toxic, biodegradable, and readily alters shape with moisture, either expanding or contracting. These expansions and contractions are normally imprecise and chaotic, but with the integration of scaffolds to direct agarose’s movement, precision and control can be achieved. Furthermore, scaffold design and integration into agarose films can be varied, being accomplished either through the externally melding of an agarose film to a scaffold during film gelation, or internally through the injection of a crystalizing solution. Agarose film composition provides a further avenue to control shape through film composition with the addition of plasticizing agents and the formation of hydrogen bonds leading to variations in bending forces. Taken together, this study aims to examine agarose films of varying composition and intermolecular forces and combine them with scaffolds of varying patterns and polymeric materials to discover the connections between film composition, scaffold design and ultimate shape morphing capabilities. To understand the structural morphology of the agarose composites, various analytical techniques will be implemented including Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), strain gauge measurements, and X-Ray scattering.

Intermission (20 min)

CELL 3924620

Top-down and bottom-up visualization of disordered regions in cellulose nanofibrils

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The nanostructure of cellulose has been hypothesized to comprise alternating crystalline and disordered (amorphous) regions, distributed along the fibril. The most notable evidence of these regions is the repeatable production of highly crystalline cellulose nanocrystals via strong acid hydrolysis. Despite decades of research on cellulose, the exact position and nature of disordered regions have not been completely discerned. They are often disregarded in nanocellulose chemistry, missing the opportunity to reap the potential for new and interesting properties originating from disordered cellulose chains. Therefore, in-depth investigation and visualization of disordered cellulose is necessary in the field of cellulose chemistry. In this work, we investigate the selective chemical modification and labeling of disordered cellulose via top-down and bottom-up approaches. In the top-down approach, labeling cellulose nanofibrils using two methods, i.e., gold nanoparticle and fluorescent labeling, is conducted and complemented with advanced microscopy, including transmission electron microscopy (TEM) and stochastic optical reconstruction microscopy (STORM). In the bottom-up approach, the labeling of hairy cellulose nanocrystals (HCNC), nanocelluloses in which the disordered regions are partially preserved, is investigated to bridge the gap between length scales and provide further information on the changes in disordered regions upon chemical modifications. The results of both approaches may lead us to believe that disordered regions are distributed semi-regularly along cellulose fibrils, becoming larger and more frequent upon further chemical modification, and acting as starting points for the formation of HCNC.

CELL 3913762

Use of ionic liquids as plasticizing agents for carbohydrate films

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In recent years, the utilization of cellulose nanocrystals (CNCs) in advanced manufacturing has surged owing to their favorable morphological and chromatic properties. These liquid crystals have a colloidal structure that promotes high crystalline alignment and order. As a result, CNCs exhibit stiffness, high surface area, and optical transparency. Although these are all excellent properties for a naturally derived biopolymer, their applications are limited due to their stiffness. Prior researchers have used synthetic polymers as plasticizing agents to reduce CNC stiffness while maintaining structural integrity. Although it has worked, the synthetic polymers have undermined other exciting properties of CNC, like its optical transparency. In this study we use a “green” alternative, ionic liquids as plasticizers. Specifically, we use two imidazolium-based ILs, which are 1-ethyl-3-methylimidazolium acetate (EMIMAc) and 1-ethyl-3-methylimidazolium chloride (EMIMCl). The introduction of an ionic liquid (IL) altered the stiffness of CNCs and conferred ion conduction properties. To understand structural changes on a fundamental level, we conducted Fourier Transform Infrared Spectroscopy (FTIR), Thermalgravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Dielectric Relaxation Spectroscopy (DRS), and X-Ray Scattering. Through these analyses, a more comprehensive understanding of morphological changes, physicochemical variations, and ion conduction has
been attained. The outcomes indicate that the utilization of various anions has caused significant modifications in the CNC's morphology and physicochemical properties.

CELL 3926461

Mussel-inspired nanocellulose coating for selective neodymium recovery

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Neodymium (Nd) plays a crucial role in the advancement of magnetic medical equipment, clean energy, and electronic devices. However, the global supply of this rare earth element (REE) is still limited, and current practices, such as solvent extraction, have negative environmental impacts. To address these issues, eco-friendly and sustainable nanotechnology for REE recovery is necessary. This work introduces a new approach using a one-step mussel-inspired nanocellulose coating (MINC) made with bifunctional hairy cellulose nanocrystals (BHCNC) containing dialdehyde and dicarboxyl groups. The dialdehyde groups facilitate dopamine-mediated orthogonal conjugation of BHCNC to microparticles, while the high dicarboxyl group content results in highly selective Nd removal, against other competitive ions such as ferric, calcium, and sodium ions. The MINC-coated substrate has fast and selective removal and recovery of Nd ions even at low concentrations. This work shows how the MINC paves the way for developing sustainable, bio-based nanocoatings that enable the recovery of REE and other precious elements.

CELL 3927088

Optimization of a green sustainable cellulose material for water purification

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Pervasive compounds including heavy metals, pesticides, and per- and polyfluoroalkyl substances are persistent in our environment and are commonly found in our drinking water. There is great need for more effective methods to remove these chemicals below their maximum contaminant level in the water we consume. Our group has developed a synthetic method to couple anion exchange polymers to TEMPO oxidized nanocellulose (TONC) through a green esterification process. Cellulose nanoresin (CNR) has been developed with intensive purification steps to yield a highly functionalized material; however, this results in a decreased mass of our product. To translate this technology to broader applications, higher concentrations of TONC and CNR are required. At higher concentrations of TONC and thus CNR, there is a lower carboxylate content and % polymer functionalization. We have shown results optimizing the yield of the synthetic process while simultaneously optimizing the efficiency of the material. This has been done through various centrifugation methods to purify TONC. Highly centrifuged and purified TONC has a carboxylate content of 1.80 mmol/g and zeta potential of -30.7 mV at 110 mg/L, where uncentrifuged TONC samples have a carboxylate content of 1.02 mmol/g.
and zeta potential of -23.0 mV at 500 mg/L. Using these samples, we will report % functionalization of polymer on the carboxylate groups of TONC utilizing conductometric titrations. We will present dynamic light scattering and zeta potential results for the CNR samples prepared from various TONC dispersions. Adsorption isotherm and kinetic data will be reported using analytes such as PFAS and chromate. This material can adsorb sodium fluorescein with a maximum loading capacity of 26.7 mg/g while maintaining high water flux of 707 Lm⁻²h⁻¹bar⁻¹. Based on preliminary results and current work, we believe this material can remove anionic contaminants from drinking water in a way that is effective and sustainable.

Symposium CELL 001B

Monday 8/14/2023 afternoon – Moscone Convention Center, Room 302, South Bldg.

CELL 3926287

Isolation of highly crystalline cellulose via combined pretreatment/fractionation and extraction procedures within a biorefinery concept

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Biorefinery schemes aim to the valorization of the whole lignocellulosic biomass. The most important step is the pretreatment/fractionation which can facilitate the downstream valorization towards value added chemicals and fuels. The aim of this work was the efficient isolation of highly crystalline cellulose from agricultural/forestry residues without “sacrificing” hemicellulose and lignin. The pretreatment/fractionation was based on different combination of hydrothermal, dilute acid, organosolv pretreatment and extraction
procedures. Hydrothermal pretreatment in neat water under relatively intense conditions (220 °C, 15 min) enhances the hemicellulose removal (up to 96%) in the liquid fraction, as xylose monomers and degradation products (organic acids, HMF, furfural). In the solid fraction, the “surface” lignin was extracted by “green” and easily recoverable ethanol (delignification 44%). Biomass loss due to humins formation was prevented by the addition of dilute sulfuric acid as catalyst during the pretreatment which allowed milder (temperature, time) conditions leading to recovery of xylose monomers with high hemicellulose removal (up to 80%). When the organosolv pretreatment in ethanol-water medium with dilute sulfuric acid was applied, hemicellulose removal and delignification were as high as 90% and 86%, respectively. The combination of dilute acid with subsequent organosolv pretreatment led also to efficient hemicellulose isolation as xylose monomers in the first step and sugar free lignin in the second step. Finally, the remaining biomass enriched in cellulose was converted to highly crystalline cellulose via bleaching process using NaClO₂/CH₃COOH media with improved thermal properties, facilitating its further transformation and utilization in polymer and resins production.

CELL 3914114

Towards negative emissions: Low-temperature fast synthesis of carbon sub-micron spheres from cellulose

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The temperature and pressure of the hydrothermal process occurring in a batch reactor are typically coupled. Herein, we develop a decoupled temperature and pressure hydrothermal system that can heat the cellulose at a constant pressure, thus lowering the degradation temperature of cellulose significantly and enabling the fast production of carbon sub-micron spheres. Carbon sub-micron spheres can be produced without any isothermal time, much faster compared to the conventional hydrothermal process. High-pressure water can help to cleave the hydrogen bonds in cellulose and facilitate dehydration reactions, thus promoting cellulose carbonization at low temperatures. A life cycle assessment based on a conceptual biorefinery design reveals that this technology leads to a substantial reduction in carbon emissions when hydrochar replacing fuel or used for soil amendment. Overall, the decoupled temperature and pressure hydrothermal treatment in this study provides a promising method to produce sustainable carbon materials from cellulose with a carbon-negative effect.
Energy harvesting from renewable materials: Harnessing the energy from moisture diffusion using biomass-derived activated carbon

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In this research, we developed a Biomass-derived Moisture Diffusion Energy Harvester (Bio-MDEH) using Biomass-derived Activated Carbon (Bio-AC) as a renewable and carbon-neutral material. Bio-MDEH was designed as a potential power source for environmental sensors that measure data remotely. Bio-AC was produced by carbonizing dried corn stover powder (5 mm or less) with activating catalyst (KOH, ZnCl₂, H₃PO₄), followed by ball milling and surface modification (acid treatment). The Bio-MDEH was prepared by coating fibrous material with a mixture of Bio-AC, deionized water, surfactant, and carbon black. Using KOH catalyzed activated carbon, we achieved the maximum performance of 926.2 mV and 37.75 μA, which is 4.6 times higher than that of carbon black MDEH. The enhancement of Bio-MDEH performance was due to the development of a mesopore structure induced from catalytic activation, introduction of hydrophilic functional groups, and improvement of electrical conductivity. Additionally, we connected both ends of the Bio-MDEH to the powering pins (Vcc, GND) of various sensors (contact/light/soil moisture sensor) and measured the voltage of the signal pin (OUT) with a multimeter (DMM7510, Keithley). Deionized water (0.05 ml) was applied onto the edge of the Bio-MDEH, followed by the sensor state manipulation. The output voltage of the sensors was respectively modified by 1.6 V, 50 mV, and 0.85 mV, resulting in detectable changes that could be measured by a micro-controller. Subsequently, multiple Bio-MDEHs that were connected in series or parallel were able to produce 1.8 V and 214 μA of electricity, leading to the successful lighting of a single LED. Our findings demonstrate the potential of Bio-MDEH as an eco-friendly and efficient energy harvester for environmental sensors. This technology could pave the way for more sustainable solutions in the field of renewable materials and energy.

Figure caption: Process steps of Bio-MDEH
CELL 3927626

Surface properties of cellulose nanocrystal anti-fog thin films

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When water droplets coalesce on transparent surfaces, undesirable fogging and visual distortions can occur. One metric for this fogging is % haze which can be measured using optical scattering techniques. We have studied the thin film properties of cellulose nanocrystal (CNC) based coatings applied to glass and polycarbonate surfaces. We prepared CNC dispersions in water/ethanol mixtures and applied these to various substrates. The CNC dispersions were cast onto glass and polycarbonate substrates, dried, and the surface characteristics of the resulting thin films were explored (AFM, optical microscopy, goniometry, hazometry). We studied film formation from the water/ethanol dispersions and also report the resulting CNC film properties. Our cellulose coating imparts excellent antifogging performance by significantly improving the hydrophilicity of the sample surfaces while minimizing the impact on visual clarity with haze values of < 2%. These coatings offer a promising antifogging strategy based on a renewable and sustainable material for real-world applications on various surfaces. Clean, dry uncoated substrates, exhibited very low haze values, with 0.19% for neat glass 1.62% for polycarbonate. Upon exposure to humidified air, where fogging might be commonly observed, visibility is severely decreased by fogging with both uncoated substrates exhibiting haze above 40%. Slides coated with CNC had dramatically enhanced AF properties with coated glass slides at 1.11% and coated polycarbonate samples at 3.60% haze when exposed to humidified air.

Figure caption: Substrates both CNC coated and uncoated exposed to humidity. Glass (A) polycarbonate (B)
Figure caption: Average haze for CNC coated and non-coated glass and polycarbonate (PC) surfaces measured using an integrating sphere hazometer (ASTM 1003.27).

**Intermission (20 min)**

**CELL 3926004**

**Fabrication of self-iron doped hydroxyapatite derived from calcium residue from steel slag for efficient photocatalytic glucose conversion**

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During the iron smelting process, a large amount of steel slag was produced, although it was mostly used in civil engineering. The remaining iron in steel slag was extracted to recover the iron, however, some solid Ca-containing residue was left over as a second byproduct. The effective use of the solid residue in cutting-edge green energy applications has been emphasized to promote sustainable development. Thus, in this work, Ca residue after iron extraction from steel slag was converted to self-iron doped hydroxyapatite (FeHAp). In addition, the extraction time of iron was optimized to vary the Fe content in the structure of FeHAp. The obtained FeHAp samples were characterized and used for the photocatalytic conversion of glucose to lactic acid, which can serve as a key substrate in a wide range of chemicals. Compared with the normal hydroxyapatite (HAp) derived from calcium oxide, the optimized FeHAp showed higher photocatalytic glucose conversion with higher selectivity of lactic product yield than pristine HAp. The enhanced rate of the photocatalytic reactions over the FeHAp was attributed to its excellent light absorption ability due to a smaller energy bandgap, higher separation, and transportation of photogenerated electron-hole pairs. Moreover, the energy-resolved distribution of the electron trap (ERDT) pattern for the FeHAp suggested the formation of a new electronic level by iron in the structure of FeHAp, which was in agreement with the optical
characterization and high photocatalytic activity. Based on the above, the photocatalytic mechanism for the conversion of glucose to lactic acid over FeHAp was proposed.

**CELL 3922402**

*Revealing the roles of biomass components in the biosorption of heavy metals*

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Lead is a heavy metal contaminant that can result in severe health problems even at ultralow concentrations. Current state-of-the-art technology relies on expensive synthetic ion-exchange resins, but hemp can be an economical and ecologically sustainable biosorbent alternative to synthetic sorbents. This study investigated removing aqueous lead(II) ions by biosorbents derived from raw and chemically treated hemp stalks. Lead(II) biosorption exhibited pseudo-second-order kinetics with intraparticle diffusion as the rate-limiting step, and the biosorption process was exothermic and favorable. Biosorbents were characterized by FTIR, SEM, and XRD to rationalize the biosorption process. Based on the biosorption capacities of various chemical-treated biosorbents, the capacities for cellulose, hemicellulose, and lignin were 277.39, 878.46, and 17.96 mg/g. Due to its hydrophilic nature and multi-functional groups, hemicellulose exhibited superior performance to commercial ion-exchange resins. The obtained results demonstrate the feasibility of using biosorbents derived from hemp stalks as sustainable and economical materials for wastewater treatment.

**CELL 3920708**

*Catalytic co-pyrolysis of pine wood and polypropylene using loess/zeolite hybrid catalyst: A study for understanding the synergistic effects of biomass and plastic co-pyrolysis*

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This research reports on the catalytic fast co-pyrolysis of pine wood sawdust and polypropylene (PP) in an analytical pyrolyzer, using loess, a common soil mineral in East Asia, as the catalyst. Co-pyrolysis of pine and PP was studied to investigate the interaction between natural biomass polymers and synthetic plastic polymers when degraded by heat and the following catalytic upgrade of the pyrolysis vapor. To enhance the performance of loess as a catalyst suitable for co-pyrolysis, it was reformed into a zeolite-like, acid-active, and well-distributed structure. The analytical pyrolysis was performed at 600°C, with 1.0 mg of feedstock and 8.0 mg of catalyst loaded, and the pyrolytic vapor was directly injected into GC/MS to determine the chemical compounds. 35-50 components were identified and classified into six groups: MAH, PAH, Phenols, Furfurals, Al-
kenes, and Alkanes. The results showed that the co-pyrolysis of pine with PP significantly decreased the oxygen content in the pyrolytic products from 23.4% (pine only) to 0.3% (pine+PP/ZSM-5), which increased the HHV of pyrolytic products from 25.9 MJ/kg to 34.4 MJ/kg. Compared to the independent conversion of pine and PP, the upgrading of pyrolysis vapor using a loess/zeolite hybrid catalyst resulted in increased yields of hydrocarbons and reduced wax formation, demonstrating a synergistic effect. In catalytic co-pyrolysis, the reduced formation of alkanes suggests that phenolic compounds in lignin function as effective hydrogen acceptors during deoxygenation. Furthermore, the loess/zeolite hybrid catalyst exhibits greater catalytic activity than mesoporous ZSM-5 in promoting decarbonylation over dehydration. The pyrolytic products produced using the hybrid catalyst show a higher hydrogen content of 9.6 wt%, compared to 6.4 wt% using ZSM-5. As a result, the H/C$_{eff}$ of the pyrolytic products over the loess/zeolite catalyst increases to 1.25, which is higher than the 0.89 value observed for ZSM-5. This indicates a greater potential for improved fuel properties using the loess/zeolite catalyst.

Figure caption: Catalytic co-pyrolysis process
Photo-curing 3D printing of biocomposites from bamboo fibers and palm oil-based resins

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The development of biocomposite from renewable reinforcements or/and matrices to replace petroleum counterparts have drawn much attention to create a sustainable society. Photo-curing 3D printing technique can achieve high precision and customization for polymer composites preparation. Considering the combination of material renewability and advanced 3D printing techniques, the present work demonstrated a simple and convenient strategy to manufacture biocomposites from micro-scale bamboo fibers (MBFs) and a vinyl palm oil-based resins via photo-curing 3D printing. To improve the dispersion and stability of MBFs in the bio-based inks and the interfacial adhesion between fibers and matrix, the MBFs were modified with methacrylic anhydride to endow the fibers with C=C bonds. The modified MBFs could participate in the crosslinking of the bio-based matrix and thus greatly enhance the mechanical strength and modulus as well as glass transition temperatures of the composites. More importantly, the matrix of the printed bio-based composites can be degraded, which is conducive to the recycling and utilization of fibers.

Figure caption: A series of biocomposites were manufactured from renewable bamboo fibers and palm oil via photo 3D printing technique.
CELL 3927136

Mechanisms and performances of physically and chemically crosslinked advanced sustainable and reusable gelatin-based hydrogel “Jelly ice cubes” coolant

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Previously, a novel cooling media called "Jelly Ice Cubes" (JICs) was proposed based on gelatin hydrogels, aimed at maintaining the safety and quality of temperature-sensitive commodities and avoiding the consumption of plastic packages. To ensure the reusability of JICs, we proposed a new environmentally friendly hydrogel tuning strategy to consolidate the 3D hydrogel network collectively using rapid-freezing-slow-thawing (RFST) treatment with photo-crosslinking induced by menadione sodium bisulfite (MSB), achieving a synergistic effect of the physical and the chemical crosslinks with unknown mechanisms. The study investigated the hydrogel tuning strategy, detailing the mechanisms and optimizing preparation conditions for enhanced JICs. It was experimentally proved that RFST treatment induced the generation of gelatin micro-crystallites, refined the protein polymeric network, and shortened the distance of potential photo-crosslinking spots. The refined hydrogel 3D network was consolidated by the photo-crosslinking reaction at the edge of gelatin micro-crystallites. The proposed crosslinking method resulted in stronger and more robust mechanical properties for JICs with stable water content after repeated freezing-thawing cycles while retaining their desired cooling efficiency and biodegradability. The proposed hydrogel tuning strategy widely applies to engineering other hydrogel materials with sustainability, biodegradability, and stability against phase changes.

CELL 3920583

Keratin/chitin composite fibers with enhanced elongation, water stability, strength, and elastic modulus

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We have created feather-based keratin/chitin composite fibers with similar toughness and wet stability to wool fibers. Regenerated keratin fibers from chicken feathers have properties similar to that of feathers, but worse than that of wool due to their lower molecular weight. Protein regenerated materials also suffer from high brittleness and low wet stability. We report an approach to substantially improve the properties of feather-based keratin fibers using chitin nanoparticles with controlled deacetylation and oxidation as reinforcement materials. Differed from conventional reinforcement of composites with increased tensile strength and elastic modules but decreased elongation, this
unique biodegradable nanoparticle improves the strength and elongation simultaneously with no need of any plasticizers. It also improves the wet stability of the fibers. Such improvement of properties is from the high compatibility between keratin and chitin, especially the partially deacetylated chitin. The amine groups and the aldehyde groups generated via deacetylation and oxidation, respectively, allow establishment of chemical crosslinkages between keratin molecules and chitin nanoparticles forming 3-dimentional networks, which provide the composite fibers with excellent strength, elongation and water stability. Compared to the virgin feather-derived keratin fibers, keratin/chitin composite fibers had at least 80%, 90%, and 100% increases in dry tenacity, dry breaking elongation, and wet tenacity, respectively, resulting in fibers with similar toughness to wool for high value applications. Due to the high compatibility between proteins and chitin, the stable 3-dimentional networks, and the excellent biodegradability, this technology can be applied to other biodegradable protein materials such as films for broad industrial applications.

**Intermission (20 minutes)**

**CELL 3920934**

**Plant proteins: new frontiers in high performance natural materials**

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Biomaterials development has traditionally focussed on carbohydrate chemistry and the integration of saccharides into existing petrochemical processing streams. The mechanical properties of polysaccharide biomaterials, and derivates that mimic petrochemical polymer chains, are derived from a combination of factors such as chain length, chain composition, and side group characteristics. Altering material properties of such carbohydrate derived materials is therefore dependent on chemical modification. This introduces losses due to process efficiency, and places the resulting materials under increased regulatory scrutiny - as they are no longer 'natural polymers'. Many biobased materials derived from carbohydrate feedstocks are now classified as plastics under EU and international regulations, such as ECHA.

But nature has another great class of polymeric materials - proteins. Unlike carbohydrate based materials, a large part of the mechanical and material properties of proteins is derived from their tertiary structure. Critically, this tertiary structure can be modified without chemical alteration of the protein itself; with dramatic results.

Xampla spun out from the University of Cambridge to exploit this highly promising and patented new class of structured protein materials. These novel natural materials are produced from plants, through a scalable, reproducible, and green manufacturing process that overcomes the solubility limitation of plant proteins, enabling production of materials with highly controlled properties through molecular self-assembly. In use, these materials offer unusually high strength (even comparable to some petroleum-based pol-
ymer such as low-density polyethylene) and excellent oxygen barrier properties (comparable to polyvinyl chloride), while at end of life, they will safely biodegrade, in marine, freshwater, or soil environments.

![Figure caption: Supramolecular engineering of proteins](image)

![Figure caption: Biodegradability comparison](image)

**CELL 3925451**

**Developing self-standing nanostructured silk fibroin films by spin coating processing and alcohol post treatment**

*Diego Gomez-Maldonado*[^1][^2], d.gomezmalodonado@northeastern.edu, *Federico Zea*[^3], *Nayomi Z. Plaza*[^4], *Carl Houtman*[^4], *Maria S. Peresin*[^1], *Adriana Restrepo-Osorio*[^3][^5]. (1) *College of Forestry, Wildlife and Environment, Auburn University, Auburn, Alabama, United States*; (2) *Department of Chemical Engineering, Northeastern University, Boston, Massachusetts, United States*; (3) *Grupo de Investigación sobre Nuevos Materiales, Universidad Pontificia Bolivariana, Medellin, Antioquia, Colombia*; (4) *USDA Forest Products Laboratory, Madison, Wisconsin, United States*; (5) *Facultad de Ingeniería Química y Agroindustrial, Escuela de Ingenierías, Universidad Pontificia Bolivariana, Medellin, Antioquia, Colombia*.

Silk fibroin (SF) has interesting properties such as mechanical robustness, biocompatibility, biodegradability, and hypoallergenic behavior, it could also be obtained from silk fibrous waste, making it attractive for biomedical, electronic, and composite applications.

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SF thin films with nanostructured architectures as free-standing nanosheets, permit to best utilize this material in applications such as packaging, electronics, or tissue engineering. An alternative to develop these films with high water stability is to increase the amount of β-sheets on the structure, which can be achieved by post generation treatment with alcohol and other solvents. A less studied impact of this post treatment is the changes on the surface rugosity, which in turn will affect the surface interactions and applicability. In this work, we generated self-standing films through spin coating, analyzing process variables such as the impact of the revolutions per minute and initial SF concentration. Post treatment with ethanol was performed and compared to untreated films. When 500 rpm were used, films between 5 to 9 µm of thickness were formed and could be separated from the base substrate. Films formed with 20% initial concentration presented more isotropy throughout the films as observed with small angle light scattering (SALS), as well as with atomic and electronic microscopies. Moreover, it was found that the spin coating did not align the SF on the surface, allowing for a uniform film. Immersion on methanol resulted in the formation of a more rugose surface for the films prepared with lower initial concentrations but had lower impact on the 20% films, despite of having an impact on the isotropy. Differential scanning calorimetry and Fourier-transform infrared spectroscopy confirmed the increase of β-sheets simply by the film formation process, more than doubling the values from 15% to 37% for the 20% initial concentration. Post treatment increased them further only 2% but decreased the standard deviation on the measurements. This work then demonstrates that self-standing stable and nanostructured films can be obtained from spin coating processing, with improved properties for its applications in novel applications.

CELL 3908796

Multifunctional tandem repeat proteins: Triboelectricity, selective absorption, and self-healing

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To reduce the environmental harm caused by traditional non-renewable polymers, this study developed biopolymer substitutes namely, squid ring teeth-inspired fibrillar Tandem Repeat (TR) proteins. TR proteins were synthesized via gene expression in E. coli and fermentation at 100L scale. Three properties of TR proteins were studied. First, these TR protein-based materials were found to be more triboelectric than most traditionally used plastics making them a sustainable solution across technologies. The proposed approach was demonstrated successfully at the laboratory scale by wet spinning of cellulose fibers carrying TR proteins, showing promise for applications needing renewable resources. X-ray diffraction and mechanical tests substantiated the compatibility of the two phases. Adding 10% protein by weight to cellulose fibers considerably enhanced triboelectric voltage output (~50%), whereas a thin coating boosted it by 98%.
Second, sessile drop experiments confirmed hydrophobicity of TR proteins with an impressive 56° difference in contact angles between oil and water. The salt leaching method enabled the preparation of highly porous (87.6 ± 1.8%) TR protein foams that showed advanced abilities, such as rapid selective oil-absorption with an efficiency of 93.9%. Finally, TR foams have proven to be a prime candidate for aerosol and water filtration processes due to their impressive self-healing properties, allowing these proteins to remain virtually unscathed despite repeated use. Furthermore, this renewability will enable them to easily transition into different applications after they've served their purpose.

Symposium CELL 001D

Wednesday 8/16/2023 - 10 a.m. to 1:50 p.m.

Attention: This is a virtual only session!!

CELL 3920882

Enhanced biomass based composites for the selective adsorption of metal ions from waters

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The extraction of metal ions (either valuable ions such as Li\textsuperscript{+} or heavy metal ions) from waters has attracted much interest as a means to meet increasing demand for lithium with the rapid expansion of the electric vehicle and electronics markets. Herein, a series of renewable and recyclable biomass (cellulose, chitosan and sodium alginate) based composites was developed and investigated toward the extraction of lithium from industrial sewage and seawaters. The porous structure of the biomass films and aerogels was characterized, and its extraction efficacy and selectivity toward lithium and heavy meal
ions from an aqueous solution (ppm level) and seawater (ppb level) were investigated. The HMO/cellulose film exhibited a higher Li\(^+\) adsorption capacity (21.6 mg g\(^{-1}\) HMO) than those reported in literature for lithium extraction, and the chitosan and sodium alginate aerogels perform excellent selective adsorption abilities for heavy metal ions (81.15, 38.87 and 38.15 mg g\(^{-1}\) for Cu\(^{2+}\), Pb\(^{2+}\) and Cd\(^{2+}\), respectively). Furthermore, the adsorption capacity and mechanical strength of the composites remained stable even after 5-10 times of adsorption–desorption cycles. The present findings demonstrate the potential of the as-prepared biomass-based composites for the recovery of a series of metal ions from seawater or wastewater.

Figure caption: Illustration of biomass-based composites for selective adsorption of metal ions

**CELL 3899478**

**Novel curcumin-silver nanoparticles-methyl cellulose nanocomposite, preparation, characterization, and medical applications**

**Manal A. El-Sheikh**, dr.manal.elsheikh@gmail.com. Chemistry, Jouf University, AlQurayyate, Al-Jouf, Saudi Arabia.

Curcumin and silver nanoparticles (AgNPs) are characterized by their antimicrobial and antiviral efficacy towards many microbial and viral infections. The current work aims at synthesizing a novel nanocomposite-based methyl cellulose (MC) and curcumin ethanolic extract, as both reducing and stabilizing agents, silver nitrate as a precursor, and water: ethanol ratio as a solvent. Curcumin ethanolic extract of was obtained by a reflux system of pure ethanol and curcumin at the boiling point of ethanol for 5 h under continuous stirring using magnetic heating mantle. Different loads of curcumin ethanolic extract, MC, and silver nitrate were applied to optimize the synthesizing conditions of AgNPs. Parameters studied were: reaction time; concentrations of MC, AgNO\(_3\), curcumin; water: ethanol ratio; Material to liquor ratio; while are reactions were performed at the boiling point of ethanol. The nanocomposite so obtained was evaluated by measuring the absorbance of the curcumin- silver nanoparticles (Cur-AgNPs) colloidal solution using UV-Visible spectrophotometer. Sample showed highest absorbance of AgNPs was further evaluated by FTIR, TEM, SEM, TGA, XRD, antimicrobial and antiviral efficacy. TEM showed polycrystalline particles with average size of about 10-22 nm.
Sustainable material for the development of multifunctional cotton fabric by L-b-L self-assembly technique

Gulshitab Aalam1, gulshitabaalam555@gmail.com, Md. Amir2, Mohammad Haider1,3, S. Wazed Ali1,4. (1) School of Interdisciplinary Research (SIRe), Indian Institute of Technology Delhi, New Delhi, India; (2) Centre for Sensors, Instrumentation, and Cyber-physical System Engineering (SeNSE), Indian Institute of Technology Delhi, New Delhi, Delhi, India; (3) Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, Delhi, India; (4) Textile Engineering, Indian Institute of Technology Delhi, New Delhi, Delhi, India.

Generation of enormous amounts of various contaminants such as debris and dredging, due to rapid construction in the present world, are primarily the reasons for overgrowth of mosquitoes, bacteria, viruses, fungi, free radicals, etc. which are the threats for the inhabitants as far as health and hygiene are concerned. Therefore, developing a sustainable solution to protect humans and animals from the free radicals and growth of such insects and microbes is the need of the hour. To overcome some of these problems, many synthetic pesticides like N, N-Diethyl-meta-Toluamide (DEET), picaridin, permethrin, etc.
are commercially available, but most of them having undesirable impacts on nature and mankind are not the lucrative solution. In this context, biomass-derived molecules are considered environmentally friendly and due to their outstanding medicinal properties, they could be a better alternative to synthetic pesticides. Moreover, multifunctional fabric are a desirable substrate to protect human beings from mosquito bites and other microbial attack as well as ultraviolet (UV) radiation as most of the parts of human body is covered by fabrics. In the present study, we developed multifunctional cotton fabric using biomass-derived coumalic acid with biocompatible branched polyethyleneimine via layer-by-layer (L-b-L) self-assembly technique. Fourier-transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy (FESEM) were used to characterize the L-b-L-coated cotton fabric. An outstanding mosquito repellence (>90%) against aedes species and outstanding antibacterial activity against gram-positive (S. aureus) and gram-negative (E. coli) bacteria (>95%) were achieved. The treated fabric was also imbued with additional functional properties such as antioxidant activity (>94%) and UV resistance (with an UPF >50). Cytotoxic study revealed that the L-b-L coated cotton fabric is biocompatible and completely safe for application. Thus, the study demonstrated that biomass-derived coumalic acid coated cotton fabric is biocompatible and apart from excellent UV resistance property, it can bestow outstanding mosquito repellent and antibacterial efficacy which are sustainable even after 25 home washings with a negligible decrement.

**CELL 3921665**

**Comparision of performance of supervised machine learning models and neural net regression for production of bioethanol from cellulosic materials using saccharomyces cerevisiae**

Vishal Murali, contact@vishalmurali.com, Anup Ashok, Arun Lanka. Chemical Engineering, Padmasri Dr BV Raju Institute of Technology, Narsapur, Telangana, India.

Bioethanol is a renewable and cost-effective alternative to fossil fuels which can be derived from various biomass sources such as corn, sugarcane molasses, and other cellulosic materials. The usage and production of bioethanol has gained traction in the recent years with a good promise for the future generations to come. In the Indian market, the gasoline outlets are beginning to transition to a 20% blend of bioethanol called E-20 with gasoline from a 10% blend. This is done to maintain the calorific value of the blend along with reducing the emission of CO (carbon monoxide) into the environment. The paper aims to produce bioethanol from cellulosic material (Psidium Gujava) using Saccharomyces Cerevisiae (S.Cerevisiae). This is achieved by first collecting the leaves of Psidium Gujava and treating them initially to enhance the content of cellulose in the stock solution. After pretreating the solution, the solution is sterilized and inoculated with S.Cerevisiae in the form of over-the-counter Bakers' Yeast. Post-fermentation, the yield is purified, and yield is measured using UV-Vis Spectrophotometer. Post the production of bioethanol, the yield concentrations are collected and interpolated to the required amount. The dataset collected in form of CSV is put through various algorithms to predict the yield. The algorithms are developed, trained, and tested in python using the sci-kit learn
module in case of Supervised learning models and in the case of neural network regression, algorithm is developed in python’s TensorFlow module using Google Colab. Regression algorithms like K-Nearest neighbours' regression, Support Vector Regression, Decision Tree regression and Random Forest Regression were some of the models in which was developed, trained, and tested and yielded a promising result with a good prediction of the bioethanol yield. Amongst the models above, the random forest regressor showed more accurate results with a cleaner prediction. Analysis of different built-in kernel types in SVR was also performed where the radial based function (RBF) kernel showed more promise in terms of accuracy but the prediction value, the rbf showed a lower yield with good accuracy than the others. This situation was not the case for the other kernels, but the accuracy dropped drastically. Apart from the accuracy values, mean squared error, average of errors, and standard deviation in errors were also taken into consideration for analysis purposes.

Intermission (20 min)

CELL 3922949

Co-gasification study of high ash Indian coal with rice husk

Alka D. Kamble, alka.kamble@gmail.com. Chemistry, KL Deemed to be University, Guntur, Andhra Pradesh, India.

Co-gasification is an emerging technology for the production of gaseous fuels, like syngas, produced from natural materials like coal and biomass allowing for economic production, effective operations and reducing the impact on the environment with optimal thermal efficiency. However, the direct use of non-renewable fuel: coal has been a concern because of the environmental impacts caused by the emission of greenhouse gases like $\text{CO}_2$ as well as the lower carbon conversion efficiency. The annual biomass production in different parts of India from various sources is >500 million tons out of which around 350 million tons are utilized in conventional routes and more than 150 million tons is still an excess quantity. However, the high alkali contents in biomass, like sodium and potassium, cause operational problems like agglomeration and clinker formation in a gasifier. These operative problems can be controlled by optimizing the blend composition of high ash coal and biomass feedstocks as well as optimizing operational parameters. In this direction, an experimental work on co-gasification of high ash coal and rice husk blends in a fluidized bed working at different temperatures and pressure is carried out in a pilot-scale fluidized bed setup at CIMFR Dhanbad using a mixture of steams and air as a gasifying agent encourages the feasibility to implement co-gasification on large scale in India, which can be one of the alternatives to produce fuel gas for its multiple applications like heating and electricity generation in near future. This study also determined the properties of rice husk and high ash coal blends and their suitability for co-gasification in a fluidized bed gasifier. A bomb calorimeter was used to determine the calorific values of the materials. CHNS and FTIR analyses were carried out to determine the elemental analysis of the material. The kinetic analysis of the feedstock has
supported the prediction of the rate at which co-gasification should be carried out. The results suggested that blending coal with rice husk results in a faster reaction rate at lower temperatures than that of coal alone as well as lower activation energy, due to the high quantity of volatile matter in biomass.

CELL 3901592

Novel cinnamon-methyl cellulose-silver nanocomposite, preparation, characterization, and cotton fabric finishing

Manal A. El-Sheikh, dr.manal.elsheikh@gmail.com. Chemistry, Jouf University, AlQurayyate, Al-Jouf, Saudi Arabia.

In addition to its pleasant aroma and flavor, cinnamon is a well-known herbal medicine. Silver nanoparticles were proved to be more efficient in their antimicrobial activities. Recently, the green synthesis of nanoparticles using plant extract and biodegradable polymers was adopted as an alternative for the hazardous chemical methods. In the current work, cinnamon bark oil, methyl cellulose, silver nitrate, and glycerol were used for the first time to synthesize cinnamon - methyl cellulose - silver nanocomposite. Doing so, synergistic effect of antimicrobial properties for both silver nanoparticles and cinnamon was achieved. The “cinnamon - methyl cellulose - silver nanocomposite” was further utilized for finishing and dyeing cotton fabrics to impart them antimicrobial properties. Parameters affecting the synthesis process namely, reaction time and temperature, and concentrations of cinnamon oil, methyl cellulose, silver nitrate and glycerol were studied. The finished cotton fabrics were tested for washing durability up to twenty washing cycles. The “cinnamon - methyl cellulose - silver nanocomposite” was characterized by UV-Visible spectrophotometer, FTIR, TEM, SEM, EDX, TGA, DSC, and XRD. Results showed that the optimum conditions for the synthesis of the nanocomposite was: 100°C; 2h; 2 g methyl cellulose; 0.5 g cinnamon oil and 1 g glycerol / 100 ml water and 0.003 M AgNO₃. UV- Vis spectra showed two bell shape beaks at about 420 nm and 290 nm characteristic for silver nanoparticles and cinnamic acid respectively. TEM and XRD results confirmed the presence of nano-crystalline Ag particles.

CELL 3926476

Experimental and theoretical studies on cellulose dissolution in mixtures of ionic liquids and molecular solvents

Omar El Seoud, elseoud.usp@gmail.com, Nicolas Keppeler, Paulo A. Pires. Institute of Chemistry, The University of São Paulo, São Paulo, São Paulo, Brazil.
We investigated the dependence of dissolution of microcrystalline cellulose (MCC), given on the mass fraction scale (m%), in binary solvent mixtures of ionic liquids (ILs) and molecular solvents (MSs). The former included 1-(n-butyl)-3-methylimidazolium cation, BuMeIm\(^+\), with acetate (AcO\(^-\)) and chloride (Cl\(^-\)) anions; the MSs used were N,N-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO). We changed the mole fraction of the MS (\(\chi_{\text{DMAc}}\) or \(\chi_{\text{DMSO}}\)) and the temperature (T). The order of maximum m% was found to be BuMeImAcO-DMSO > BuMeImAcO-DMAc >> BuMeImCl-DMSO. To rationalize this dependence, we used molecular dynamics (MD) simulations employing, as a model for MCC, a crystallite of eight chains, each containing ten anhydroglucose units (AGUs). Values of the root-mean-square-deviation (RMSD) showed that decamer-chain separation follows the same order as the maximum m%; more chain separation indicates greater crystallite dissolution. Additionally, the values and the sharpness of the peaks of the radial distribution function, g(r) followed the same order of dissolution, primarily due to the IL-anion hydrogen bonding with the hydroxyl groups of the AGU. We also recorded the turbidity of MCC-IL-DMSO solutions and the conductance of cellulose-IL-MS solutions; the results of both experiments corroborated our interpretations of the MD results. Thus, MD simulations can be employed as “screening tool”, this saves labor and material in the search for optimal solvents for cellulose dissolution.

**CELL 3928311**

**Biodegradable water-borne emulsions for paper coating**

*Muhammad Rabnawaz, rabnawaz@msu.edu. Packaging, Michigan State University, East Lansing, Michigan, United States.*

We have developed a waterborne acrylated epoxidized soybean oil (AESO) blend in the presence of biocompatible polyvinyl alcohol (PVOH) as an emulsifying agent. This emulsion was then cast onto the surface of kraft paper, and subsequently UV cured, thus imparting the substrate with excellent oil/water repellency. The water absorptivity measurement tests revealed that the coated paper has excellent Cobb600 and Cobb1800 values of ~9 and ~13 g/m\(^2\), respectively, as well as a kit rating of 7/12. The AESO loading was optimized, and the best performing sample had a loading in the range of ~15-20 g/m\(^2\). It was found that the coated paper retained >85% of the tensile strength exhibited by the uncoated paper. Other mechanical parameters measurements such as ring crush test (RCT), bending stiffness (BS), and internal tearing resistance (ITR) illustrate >90% retention in their performance with respect to uncoated paper.
Symposium Separates

CELL 003 “Emerging Technologies and Applications of (Nano)Cellulose”

Organizers
Peresin, Maria, Auburn University; Liebner, Falk Wolfgang, Boku University Vienna; Ozcan, Soydan, Oak Ridge National Laboratory; Li, Kai, Oak Ridge National Lab; Lucia, Lucian, North Carolina State University.

Symposium CELL 003A (Hybrid)
Wednesday 8/16/2023 morning – Moscone Convention Center, Room 302, South Bldg.

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<td>Slot die coating as an industrially scalable method for depositing nanocellulose dispersions onto glass fiber fabrics</td>
<td>Kim Anh Pham1, <a href="mailto:kpham47@gatech.edu">kpham47@gatech.edu</a>, Kyriaki Kalaitzidou2,1, Tequila A. Harris2, Robert J. Moon3,1. (1) School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; (2) George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; (3) US Department of Agriculture Forest Service, Washington, District of Columbia, United States.</td>
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<td>in-situ synthesis of hybrid TC-CoSe/nanocellulose quantum dots and their ... Ceron, Jhonny</td>
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<td>Development of nanocellulose-reinforced polymeric adhesives/coatings with PSOCHIA, ELENI</td>
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<td>Pickering emulsions and hydrophobized films of amphiphilic cellulose nanofibers</td>
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CELL 3915106

Slot die coating as an industrially scalable method for depositing nanocellulose dispersions onto glass fiber fabrics

Kim Anh Pham1, kpham47@gatech.edu, Kyriaki Kalaitzidou2,1, Tequila A. Harris2, Robert J. Moon3,1. (1) School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; (2) George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; (3) US Department of Agriculture Forest Service, Washington, District of Columbia, United States.

Cellulose nanomaterials are a novel class of renewable biopolymers exhibiting unique properties which have allowed research into their applications to flourish in many industries including glass fiber-reinforced composite (GFRC) manufacturing. Prior research has shown that the addition of nanocellulose sizing onto glass fiber surfaces enhances the interfacial interactions between the fibers and the polymer matrix resulting in improved mechanical properties. However, the technology used for depositing nanocellulose dispersions onto fiber rovings has struggled with scalability, coating homogeneity, and limited coating penetration through packed fibrous networks.

This study demonstrates the use of slot die coating as an industrially scalable method
for depositing cellulose nanocrystal (CNC)-epoxy emulsion coatings onto knit unidirec-
tional S-glass fiber fabrics. By determining a set of coating parameters within the operat-
ing limits, slot die coating can continuously and fully wet a glass fiber fabric substrate,
producing consistent thin film coatings on individual fibers. The coating composition,
morphology, and distribution are characterized using thermogravimetric analysis (TGA)
and scanning electron microscopy (SEM). Glass fiber-epoxy resin laminates are pro-
duced using the coated fiber fabrics and their quality is examined using SEM and optical
microscopy.

Using this methodology, the resulting slot die coated fibers all exhibit good coating ho-
mogeneity throughout the full depth of the fabric. Furthermore, more viscous solutions
containing higher concentrations of CNC were successfully deposited with good surface
morphology. Coatings containing low concentrations of CNC did not hinder fiber separa-
tion and resin wetting during laminate production.

CELL 3925441

In-situ synthesis of hybrid TG-CdSe/nanocellulose quantum dots and their use as
metal chemosensors

Jhonny M. Ceron, maoceron@outlook.com, Daniel A. Amaya-Garcia, Marianny Y.
Combariza, Cristian Blanco-Tirado. Chemistry, Universidad Industrial de Santander, Bu-
caramanga, Santander, Colombia.

Quantum dots (QDs) are light-emitting inorganic semiconductor materials with unique
electronic and optical properties, such as high quantum yields, elevated resistance to
photodegradation, broad extinction spectra, and narrow and tunable fluorescence emis-
sion. QDs find uses as photocatalytic, light-harvesting, and sensing materials. Typically,
an organometallic synthetic route delivers highly crystalline and monodisperse QDs.
However, this synthetic procedure usually requires high reaction temperatures as well as
the use of toxic reagents like trioctylphosphine oxide (TOPO), trioctylphosphine (TOP),
or hexadecyl amine (HAD). Alternative greener methodologies involving less toxic rea-
gents as capping agents (e.g., 3-mercaptopropionic acid, 1-thioglycerol, and glutathi-
one), water as a solvent, and low temperatures can also yield highly crystalline QDs.
Nevertheless, these strategies still require using reducing agents, like NaBH₄, cataloged
as toxic.

TEMPO-oxidized cellulose nanofibers (TOCN) are widely used to develop hybrid func-
tional materials. TOCN can perform as reducing agents for the in situ synthesis of Ag,
Pt, Au, and Pd nanoparticles, as reported in the literature. Still, no reports exist on using
TOCN as a reducing agent for synthesizing semiconducting quantum dots (QDs).
In this study, we report the simultaneous use of TOCN as a capping and reductive agent
for thioglycerol-CdSeQDs (TG-CdSe QDs) synthesis. We carried out a one-pot synthe-
sis in aqueous media at 100 °C and followed the influence of reaction time on crystal
growth and CdSe-TG/TOCN QDs size. After thirty minutes of reaction, TG-CdSe/TOCN
QDs reached a crystallite size of 3.93 nm. We tested TG-CdSe/TOCN QDs as
chemosensors using absorption and fluorescence spectroscopy. The hybrid material dis-
played high selectivity and sensitivity toward the detection of copper ions (Cu²⁺).
Development of nanocellulose-reinforced polymeric adhesives/coatings with nanostructured surfaces

ELENI PSOCHIA¹,², epsochia@gmail.com, Antigoni Margellou¹,², Stylianos Torofias¹,², torofias@gmail.com, Dimitrios Gkliopoulos¹,², Emmanouil Karagiannidis³, Eleftheria Athanasiadou³, Nikolaos Kehagias⁴, Konstantinos Triantafylidis¹,². (1) Department of Chemistry, Aristotle Panepistemio Thessalonikes, Thessaloniki, Central Macedonia, Greece; (2) Center for Interdisciplinary Research and Innovation, Aristotle Panepistemio Thessalonikes, Thessaloniki, Central Macedonia, Greece; (3) Chimar Hellas SA, Thessaloniki, Thessaloniki, Greece; (4) Institute of Nanoscience and Nanotechnology, Ethniko Kentro Ereunas Physikon Epistemon Demokritos, Athens, Attiki, Greece.

Biomass-derived materials are replacing petroleum derivatives leading the pathway to more sustainable and biorefinery-based technologies. In this context, cellulose, lignocellulosic biomass’s main component, is receiving increasing interest owing to its abundant nature and its biodegradable and renewable character. Particular attention is drawn to its nano-derivatives, cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs), which can be produced by mechanical or chemical treatment of cellulose, respectively. Features like high crystallinity, large surface area, optical transparency, high tensile strength and high elastic modulus as well as good mechanical properties and thermal stability, render nanocellulose an excellent candidate for polymer reinforcement. In this work, cellulose nanoparticles were produced from both commercial and agricultural biomass isolated cellulose, following various mechanical and chemical treatments. Namely, CNFs were produced by sonication treatment, while CNCs by following a typical acid hydrolysis procedure. All the materials were characterized as to their structure, crystallinity, surface area and thermal stability. In addition, their particle size as well as their morphology were assessed. The respective nanocelluloses were utilized as reinforcing additives in various polymeric substrates, such as urea-formaldehyde resins, epoxy resins and furanic resins. The surface of the nanocomposite materials was subsequently fabricated.
with nano/microstructures via nanoimprint lithography. The implemented topographies were aiming to enhance the materials’ hydrophobicity and induce antibacterial properties. The results show the successful production of nanocellulose from various lignocellulosic sources and its high potential as a reinforcing agent when also combined with nanoimprint lithography, setting groundwork to produce green and sustainable, nanoscale enhanced materials.

Intermission (20 min)

CELL 3926296

Preparation, functionalization, and improvement of different cellulosic materials and their applications in different fields

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Nowadays, it is highly demanded to improve the properties of cellulose-based materials so that they can compete and replace unsustainable materials such as fossil-based materials. In our research group, we apply different methods and strategies to improve and give different functionalities to the cellulosic materials.

The first area is mimicking the plant cell wall to immobilize dual-catalyst systems using functionalized microcrystalline cellulose or nanocelluloses. For example, artificial plant cell walls (APCWs) were assembled, which contained both lipase enzymes and metal nanoparticles. Next, the APCWs were used as heterogeneous catalyst for dynamic kinetic resolution of racemic chiral primary amines to give the enantiomerically pure amides in high yields.

Since pure cellulose-based materials are water sensitive and disintegrate in an aqueous environment, giving super hydrophobic properties to the cellulosic materials is another area we are studying. In our group, an eco-friendly and fluorine-free water-based composition has been designed for creating superhydrophobic and cellulose-based materials with the contact angles>150°. Moreover, other methods like using natural compounds like betulin or a combination of organosilanes with green organocatalysts were employed to make hydrophobic cellulose-based materials.

The third subject is about improving mechanical properties of different cellulosic materials. We have shown that the synergistic combination of polyelectrolyte complexes (PEC) and organocatalysis improved the mechanical properties of different pulps. The concept was expanded by integrating it with low-dose sulfite pre-treatment of wood chips in CTMP preparation (chemo-thermomechanical pulp). Therefore, CTMP made by preliminary sulfite pre-treatment was next surface engineered by synergistic combination of PEC and organocatalysis using organic acids as catalysts. The CTMP pulps, which contain 0.1-0.24 wt.% sulfur, prepared by our novel pulp-engineering method shows a significant Z-strength increase up to 100% compared to no surface engineering. While only sulfite pre-treatment and PEC surface engineering could improve the strength properties, it was only when the organic catalysts were present that the highest strength improvement was reached.
Hydrophobized cellulose nanocrystals through Pickering emulsion for the mechanical reinforcement of thermoplastic elastomer composites

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A hydrophobization strategy on cellulose nanocrystal (CNC) surfaces was developed through Pickering emulsion method using n-tetradecenyl succinic anhydride (TDSA) dissolved in cyclohexane as an oil phase. The CNC-stabilized Pickering emulsion was prepared through combining a charge-screened CNC suspension (0.2 wt %) and a TDSA solution (10 wt % in cyclohexane), which was then lyophilized, and reacted at 130 °C for 24 h. TDSA was well-discovered on the CNC shell after the lyophilization and then grafted onto the surface through an esterification, resulting in CNC-g-TDSA homogeneously dispersed in chloroform with 274 ± 92 nm in length and 23 ± 9 nm in width. The microstructures of the CNC-stabilized Pickering emulsion and its surface morphology after freeze-drying was investigated. The CNC-g-TDSA film showed hydrophobic characteristic (90° based on water contact angle). The nanocomposite films composed of the hydrophobized CNC and styrenic thermoplastic elastomer (TPE) were prepared by solvent casting, and characterized for the mechanical (tensile) and morphological properties (Figure 1). The nanocomposite films showed max. 4-fold increase in Young’s modulus, relatively maintaining the strength and strain at break of the neat TPE. The matrix-filler interface adhesion between CNC-g-TDSA and the TPE was demonstrated, also suggesting that the hydrophobized CNC can be used for the reinforcement of PLA thermoplastics.

Figure caption: CNC hydrophobized by TDSA and the reinforcement of SIS/CNC-g-TDSA nanocomposite.
Anisotropic cellulose nanocrystalline sponge sheets with ultrahigh water fluxes and oil/water selectivity

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Oily sewage caused by oil spill accidents has become a severe problem in the last decades. Hence, two-dimensional sheet-like filter materials for oil/water separation have received widespread attention. Porous sponge materials were developed using cellulose nanocrystals (CNCs) as raw materials. They are environmentally friendly and easy to prepare, with high flux and separation efficiency. The 1,2,3,4-butane tetracarboxylic acid cross-linked anisotropic cellulose nanocrystalline sponge sheet (B-CNC) exhibited ultrahigh water fluxes driven by gravity alone, depending on the aligned structure of channels and the rigidity of CNCs. Meanwhile, the sponge gained superhydrophilic/underwater superhydrophobic wettability with an underwater oil contact angle of up to 165.7° due to its ordered micro/nanoscale structure. B-CNC sheets displayed high oil/water selectivity without additional material doping or chemical modification. For oil/water mixtures, high separation fluxes of approximately 100,000 L·m⁻²·h⁻¹ and separation efficiencies of up to 99.99 % were obtained. For a Tween 80-stabilized toluene-in-water emulsion, the flux reached more than 50,000 L·m⁻²·h⁻¹, and the separation efficiency was above 99.7 %. B-CNC sponge sheets showed significantly higher fluxes and separation efficiencies than other bio-based two-dimensional materials. This research provides a facile and straightforward fabrication method of environmental-friendly B-CNC sponges for rapid, selective oil/water separation.
Silver-promoted decarboxylative polymerization: A green and versatile approach to graft polymers from nanocellulose

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Chemical modification by graft polymerization is an efficient and facile approach to tailor the chemical and physical properties of nanocellulose. To date, a range of polymers has been reported to be successfully grafted to nanocellulose via various polymerization routes, imparting unique properties such as stimuli-responsiveness, change in solubility and others. These methods are proven to be highly efficient, albeit requiring quite complex pre-functionalization steps to graft the polymers. Here, we report a green and versatile method to polymerize a family of vinyl monomers from the surface of oxidized cellulose nanofibers (CNFs). A robust, one-pot polymerization method was developed to graft a range of polymers from TEMPO-oxidized CNFs surface via silver(I)-promoted decarboxylative polymerization. This method relies on the oxidative decarboxylation of carboxylic acid groups to initiate free radicals on the surface of CNFs. The polymerization reaction employs a relatively mild reaction conditions and can be performed in one pot. Unlike ether or ester bonds commonly formed in other polymerization reactions, this reaction forms a C-C bond between CNF and the polymer. The properties of the polymers grafted from CNFs can be controlled by altering the silver concentration. Grafting poly(N-isopropylacrylamide) (PNIPAM) from CNFs, for example, allows the preparation of hydrogels with tunable thermo-responsive and rheological properties. Polycrylic acid (PAA)-grafted CNFs with varying degrees of branching can be also produced and developed into superabsorbent hydrogels which exhibit excellent water-retention properties. This polymerization method allows the engineering of nanocellulose into advanced functional materials for many specific applications.
Modular functionalization of oxidized cellulose through azetidinium chemistry

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Cellulose has been broadly used as a source of building materials due to the unique mechanical and chemical properties that arise from its hierarchical organization. Crystalline nanocelluloses (i.e. cellulose nanocrystals – CNCs, and cellulose nanofibrils, CNFs) not only exhibit the expected enhanced mechanical properties, but also display unique optical, electric, piezoelectric, and magnetic properties that are not found in macroscale cellulosic materials. These unique properties, along with their biodegradability and cytocompatibility, make nanocelluloses excellent candidates for the development of new advanced and environmentally benign materials. In particular, carboxylated nanocellulosic materials present better dispersion in polar solvents and offer the possibility of targeted functionalization with controlled degrees of substitution. However, most surface functionalization of carboxylated nanocelluloses is performed through processes that are expensive or require multiple lengthy steps. Our group has pursued modular surface functionalization approaches, based on azetidinium chemistry, that allow us to tune the interfacial properties and reactivity of a broad range of carboxylated cellulose nanomaterials.

In this presentation, I will describe our efforts aimed at developing a range of small molecules that can be grafted onto carboxylated cellulosic materials. Examples of the use of these surface modifications to tag nanocelluloses with organic dyes for high-resolution fluorescence microscopy, to modify paper properties, and to develop new 3D printable hydrogel resins will be presented. The ability to tune the interfacial chemistry of carboxylated nanocellulose with simple one-step grafting reactions opens the door for the use of these functional cellulosic materials in a range of applications, including paper-based microanalytical devices, and 3D printing, among many others. In addition, the ability to
apply such modular approaches to functionalize other polysaccharides make them attractive routes for the development of green materials and composites with unique properties and functionalities.

**CELL 3924947**

**Grafting to approach to realize semiconducting cellulose via click chemistry at oil/water interface**

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Fabrication of organic electronic devices using new materials and processes is the key to closing the performance gap between organic electronics and their silicon-based counterparts while also expanding their advantages in terms of cost, scalability, and sustainability. We believe that by introducing cellulose nanocrystals (CNCs) to the active layer we can dramatically reduce the amount of semiconducting polymer (SCP) necessary and take advantage of the strong mechanical properties of CNCs to strengthen the active layer and boost its durability. Building upon our previous work on CNC modification for electronic applications and cross-linking of SCPs via thiol-ene click chemistry under mild reaction conditions, we functionalized CNCs via a “grafting to” approach and applied them to a proof-of-concept OLED. We successfully adapted a process to attach cysteine on the surface of CNCs. Unlike conventional methods which require a solvent exchange process that disperses CNCs into an organic solvent, we were able to bypass this step and click styrene-capped poly (9,9’ dihexyl-fluorene) onto the surface of cysteine-modified CNCs at the oil/water interface. Our method enables us to access a larger surface area of the CNCs promoting a higher number of reactive sites. Due to their challenging processability, chemical modifications realized on CNCs are notoriously troublesome to quantify. We were able to characterize our products via IR, solid-state 13C NMR and elemental analysis. In addition, we conducted AFM and mechanical testing of the modified CNC thin layers and measured I-V-L curves of the OLEDs. The use of CNCs, amino acids, and thiol-ene click chemistry opens the door for a sustainable and scalable process to design novel organic electronic devices.

Figure caption: Synthesis of semiconducting Cellulose Nanocrystals at oil/water interface via thiol-ene click chemistry
Click chemistry meets nanocellulose: Grafting biobased phenolic esters on cellulose nanocrystals for anti-UV applications

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In this study, a new and innovative synthetic route to decorate CNCs with UV-absorbing phenolic esters is presented. A set of alkyne-modified p-hydroxycinnamate mono- and di-esters (coumarate, ferulate, and sinapate) were synthesized and grafted on azide-bearing cellulose nanocrystals via click-type copper-catalyzed azide/alkyne cycloaddition (CuAAC) reaction. The chemical route developed allowed the preparation of phenolic ester-grafted CNCs with excellent UV-absorbing properties and photostability. The degree of substitution and chemical properties of the modified CNCs are highly influenced by the structure of the phenolic ester grafted. These phenolic ester-grafted CNCs were further engineered as anti-UV fillers in hydrophilic polymeric films and cosmetic formulations. The grafting of hydrophobic phenolic ester moieties on CNCs significantly aids their dispersion in these aqueous matrices. Polyvinyl alcohol (PVA) films loaded with 20 wt% diethyl ferulate-grafted CNCs (CNC-DEF) were photostable and exhibited complete UV protection (0% transmittance) and high transparency in the visible region (70-90% transmittance). CNC-DEF-loaded PVA films also displayed remarkable mechanical and oxygen-barrier properties. Glycerol-based creams incorporated with diethyl sinapate-grafted CNCs (CNC-DES) displayed excellent UV-blocking and antioxidant activities. Cytotoxicity measurements revealed the CNC-DES not to cause significant cytotoxicity to murine fibroblast cells after 24 h of exposure. This study demonstrates the exceptional potential of phenolic ester-grafted CNCs as nature-inspired UV-filters in the next generation of packaging materials and cosmetic formulations.

Lignocellulosic biomass conversion via dual oxidation: Toward highly functional and sustainable nanomaterials

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An important pillar of sustainable development is the preparation of functional materials derived from renewable resources. Nevertheless, facile methods to convert lignocellulosic biomass to value-added, highly functional micro- and nanomaterials remain limited. Here, we use dual oxidation to convert a variety of lignocellulosic biomass into highly charged products. We show how the sequential oxidation of both delignified (e.g., softwood pulp and cotton) and untreated (e.g., raw corncob and tomato peel) lignocellulosic sources yield three distinct products, including nanoparticles, fully solubilized polymers, and microproducts, bearing up to 6 mmol of carboxylate groups per gram, which is >500% beyond the theoretical charge content of cellulose nanocrystals (CNC). As a proof-of-concept for the applications of these materials, we use carboxylated cotton microproducts to remove ~92.5 mg of neodymium (Nd) per gram from a dilute Nd solution in less than 5 min and recover approximately 64% of it via pH adjustment. We also utilize this dual oxidation to nanoengineer the redispersibility of CNC by tailoring the colloidal repulsive forces. Electrostatic and steric repulsion was imparted to CNC via two layers of disordered cellulose chains on each end (hairs) bearing a high density of dicarboxylate groups (up to ~5 mmol g⁻¹). Such anionic hairy cellulose nanocrystals (AHCNC), synthesized by the preferential oxidation of disordered regions in cellulose fibrils, attain extraordinary redispersibility compared with conventional CNC, even at high initial concentrations, high ionic strengths, and extreme pH conditions. This dual oxidation procedure provides a facile and sustainable method to nanoengineer various types of lignocellulosic biomass into highly functional nano- and micro-materials.

**Intermission (20 min)**

**CELL 3915105**

**Incorporating cellulose isolated from algae residues into polystyrene-based honeycomb structured membranes**

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Honeycomb structured porous membranes are polymeric tailored designed materials prepared via the bottom-up breath figure technique that uses water condensation droplets as molds for structuring pores. The hexagonally arranged membranes obtained with this method are of great interest for tissue engineering, drug delivery amongst other technological applications. In this work, porous membranes from either blends or composites of cellulose and polystyrene were obtained with the breath figures technique from CS₂ solutions. Composites were prepared with commercial microcrystalline cellulose or using isolated cellulose from Gelidium sp algae residues extracted with an alkaline method and later integrated with the styrene during its polymerization. Solutions (10 mg/mL) were cast inside a custom-made controlled humidity chamber. Different conditions such as relative humidity, air convection and surface preconditioning were evalu-
ated during the formation of the membranes. The quality of the hexagonal array was assessed by analyzing SEM images with a Quantitative Virtual Light Scattering (QVLS) Technique. The best membranes were obtained with the algal cellulose materials either in mixture or composite with a preconditioned surface and no airflow at 90% RH for the blend 90% RH and 95% RH for the composite. From the QVLS analysis the resulting membranes from the blend presented homogeneity and pore distribution of 0.09 and 5.81 respectively, indicating a high hexagonal structure with similarity in pore size but differences in the angle of arrangement. Conversely, the composite membranes resulted in homogeneity and pore distribution of 0.11 and 4.52 showing less similarity in pore size but better angle spacing. This work shows that isolated algal cellulose can interact with polystyrene to enhance the potential use of these structured membranes in bio-based applications through the properties and chemical versatility of cellulose.

CELL 3926463

**Organocatalyzed ring opening polymerization of ethylene brassylate in the presence of cellulose nanofibrils**

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Nowadays, the demand to reduce the dependence on fossil based materials by replacing them with biobased polymers is significantly increasing. Ethylene brassylate is a macro lactone that can be extracted from castor oil and proposes an economical way to alternative counterparts such as ε-caprolactone. Moreover, its natural origin enables us to prevent dependence on fossil-based resources. In this work, the ring opening polymerization of ethylene brassylate in the presence of an organic catalyst (1,5,7- triazabicyclo [4.4.0] dec-5- ene (TBD)) and cellulose nanofibrils (CNF) were investigated. CNFs were prepared through an environmentally benign one-step mild reaction method to fabricate lactic acid ester functionalized cellulose nanofibrils from wood-derived pulp fibers. This was done by converting pulp fibers to nanofibrillated cellulose lactate using lactic acid as both the reaction media and catalyst. Another type of CNF also was prepared by removing lactate groups from the fabricated nanofibrillated cellulose lactate. Next, the polymerization of ethylene brassylate was carried out via reactive extrusion in a micro compounder. Different conditions were investigated, and it was observed that using ethylene brassylate : TBD with molar ratio of 42 : 1, and CNFs (1 wt. %), the conversion reach to 98 % after 30 min of extrusion and the molecular weight for material was around 19 kDa. The fabricated polymeric materials were stiff and brittle, however, it was possible to injection mold them into specimens for mechanical tests.
Synthesis of protein nanocomposites reinforced by surface-modified cellulose nanocrystals

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As cellulose is the most abundant biopolymer in plant biomass, selective acid hydrolysis of plant biomass can yield biocompatible, renewable cellulose nanocrystals (CNCs). CNCs feature a large surface area, high aspect ratio, and a substantial capacity for surface chemical modification. CNCs have outstanding mechanical strength for bearing loads from external environments, with a modulus of 50-200 GPa. Therefore, incorporating CNCs into a nanocomposite matrix can potentially result in outstanding mechanical behaviors of the nanocomposites. In this study, plant biomass-derived CNCs will be used as reinforcing fillers in the nanocomposite matrix of soy protein and recombinant spidroin-amyloid-mussel foot protein as a potential candidate for food packaging or bio-adhesive applications. Nanocomposites of CNCs and CNCs with surface coating (i.e., polydopamine coating) designed to leverage intermolecular interactions with protein matrices can be used to understand the CNC surface effect. The resultant polydopamine-coated CNC-protein nanocomposites were shown to have enhanced Young’s modulus and tensile strength due to the intermolecular interactions that can modify protein properties. Mechanical modeling of the nanocomposites was applied to explain the reinforcing behavior of the surface-modified CNCs based on the tensile testing data of the nanocomposites.
CELL 3892766

**LIMINA : Lignin from Micro to Nanosize**

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Lignocellulosic biomass is a complex and resistant plant material, mainly made up of the three polymeric fractions that are cellulose, hemicellulose and lignin, which are highly entangled. Within the framework of this project, we are particularly interested in the under-valued lignin polymer which is mainly used by thermal valorization while it contains monomers with high added value. Lignin is in fact a generic term which gathers a wide family of biopolymers with aromatic skeleton. It is renewable, biodegradable, very abundant (it is the second most abundant biopolymer on earth after cellulose), and it constitutes 30% of the nonfossil organic carbon in nature. Thanks to their aromatic structure, these lignins have many properties (biocide, antioxidant, UV-light blocker...) which could be useful in wide range of technical applications.

LIMINA project will first focus on the extraction of macrolignin from forestry waste (hardwood and softwood) by the mean of eco-friendly processes (organosolv and steam explosion). The second step will be the optimization of the macrolignin size reduction by using anti-solvent precipitation with high-shear and ultrasonic homogenization processes. The last step of the project will finally be the lignin valorization through two applications: a new material property to improve the durability of biobased plastic materials.
Lignin orientation on surfaces

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Lignin is a byproduct from paper industries and biorefining processes. Due to its multifunctionality ranging from ultraviolet protection ability to thermosets, lignin represents an ideal renewable alternative for fossil-based aromatic materials, thus contributing to a sustainable biomaterial utilization. In a novel approach, we are exploring the potential of lignin as protective and mechanically stable coating. Aiming at scalable industrial processes, we investigate spray deposition as method of choice to fabricate thin lignin films and investigate the influence of different lignin fractions from different biomass sources on the molecular orientation of lignin on surfaces. Acetone and tetrahydrofuran showed different solubilities of lignin. The nanoscale and molecular structure and morphology of the spray-deposited thin films were investigated via grazing incidence small- and wide-
angle X-ray scattering (GISAXS, GIWAXS). The molecular orientation of the phenyl ring of lignin was found to be dominated by parallel sandwich stacking and depends on the solvent used. The surface properties of the thin lignin films were probed by dynamic contact angle measurements and revealed both hydrophobic and porous properties. The porosity of the thin lignin films depends on the solvent used and thus the drying kinetics and is correlated with the nanostructure derived from GISAXS. Our results show that lignin can be used as a sustainable material for water-resistant barrier films.

CELL 3934657

Unlocking the surface composition and core-shell structure of lignin nanoparticles through advanced 1H NMR techniques for biomedical and cosmetics applications

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Lignin, a highly abundant natural polymer, possesses unique structural, biodegradable and biocompatible properties, making it an ideal candidate for generating nanoparticles for targeted therapy applications, for uses in cosmetics and other personal care products. This study presents an innovative 1H liquid-state NMR spectroscopy approach, combined with transmission electron microscopy and dynamic light scattering, to investigate the surface composition, core-shell structure, and formation mechanism of lignin nanoparticles (LNPs) derived from spruce and eucalyptus kraft lignin fractions with narrow molecular weight distribution. Utilizing presaturation and excitation sculpting, the modified NMR technique revealed methoxy groups from syringyl and guaiacyl units as the main surface components, along with the existence of a shell and core structure. The results highlighted the strong dependence of LNPs on their inherent lignin properties, emphasizing the importance of selecting appropriate starting lignin materials for specific applications. As a demonstration of potential biomedical applications, LNPs showed efficacy in liver cancer treatment, exhibiting dose-dependent inhibition of hepatocellular carcinoma cell proliferation without affecting cholangiocarcinoma cell growth. This study not only underscores LNPs promising attributes, such as tailored surface functionality and low toxicity, but also showcases the development of a unique 1H NMR technique for in-depth analysis of LNPs, paving the way for the creation of advanced bio-based delivery tools for combination therapy in medicine and various applications in the personal care industry.

CELL 3927540

Demethylation of sulfonated kraft lignin for application in Phenol Formaldehyde adhesives

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Phenol-formaldehyde (PF) resin is a synthetic resin that is widely used as an adhesive in the industrial production of exterior—grade plywood panels, oriented strands of board
panels and particleboard. Despite its excellent performance in bonding strength, chemical stability, durability and low production cost, it is an environmentally unfriendly chemical derived from petroleum products. As a result, there has been considerable interest in finding a sustainable alternative for PF resins. Lignin is a promising substitute as it is a natural polymer that is obtained from lignocellulosic resources and can be converted to phenols thanks to its chemical structure. The demethylation of lignin is a known strategy to produce phenol for PF resin manufacturing. However, the current strategies are solvent-based reaction systems that are not attractive. To address this challenge, this study discusses the generation of partially sulfonated lignin and demethylation of sulfonated lignin in aqueous-based systems to generate phenols. Two types of sulfonated lignin (sulfoethylation and sulfobutylation) were utilized in this work. The impact of charge density, sulfonation type and molecular weight of sulfonated lignin on its demethylation performance for the phenol generation was studied comprehensively. This presentation will discuss how the physicochemical characteristics of lignin were altered via sulfonation and demethylation based on the results of HSQC and P NMR, XPS, FTIR and GC-MS. Also, the charge density, molecular weight and solubility of the lignin derivatives were measured and related to the performance of the reactions. This presentation discusses how sulfonation can be considered as a strategy to improve the performance of demethylation reactions in an environmentally friendly manner.

Intermission (20 min)

CELL 3927127

Aminated lignin nanoparticle formation and characterization

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Lignin is a versatile compound with tremendous unexplored potential for sustainable material fabrications. Owning to various functional groups available on its surface, lignin can be readily modified in various grafting, polymerization, depolymerization, catalytic reactions to attain enhanced properties. This effect is further intensified when the functionalized lignin particles are converted to nano size and hence, the generated material has a high surface area, reactivity and binding efficiency to other materials in composites. The focus of this study is to produce functionalized lignin via amination process. By adapting solvent exchange method, aminated lignin nanoparticles are obtained through a self-assembly mechanism. The final cationic lignin nanoparticles will be characterised to obtain full insight into the structure of the nanoparticles in terms of their size, stability, porosity, shape and rigidity. This overall goal of this study is to provide comprehensive analysis on the generation of aminated lignin nanoparticles for its potential use in coating materials for biomedical and packaging purposes. The outcome of our work will be supported with results from zeta potential analysis, stability analyzer, QCM-D, SEM and AFM.
Lignin-derived polymers for additive manufacturing

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Green alternatives to petrochemicals in manufacturing are critical avenues in trying to move towards a more sustainable economy. Additive manufacturing (AM) is one of the most important industries where green alternatives may gain traction, in part due to the field’s rapid growth. For reactive photopolymer resins and inks, there are no good sustainable alternatives available, despite natural products such as lignin derived materials offering excellent functional handles for exploitation in photopolymer 3D printing. Here we will focus on alternative approaches to petrochemicals by designing polymer resins and inks which have greener profiles compared with their contemporaries, including the use of lignin-derived monomers and polymers. Considerations will include the photopolymer and reactive diluent design, and how biomass-derived materials may even further be the route towards functional materials. Lifecycle considerations, including the degradability and recycling potential, are considered, providing insight on how sustainability and physical properties relate.

High-throughput lignocellulosic biomass characterization: Leveraging thermogravimetric analysis to screen lignin content and predict deconstruction yields

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Herein, we report a thermogravimetric analysis (TGA) method to rapidly and reliably characterize whole lignocellulosic biomass (LCB). Biomass characterization is a crucial step in the valorization of LCB as it can inform feedstock selection, guide process decisions, and enable economic/environmental optimization; however, the heterogeneity and compositional variation among LCB feedstocks remains a significant hurdle to accurate biomass compositional measurements, especially with respect to lignin. The standard approach is a National Renewable Energy Laboratory (NREL) comprehensive laboratory analytical procedure, which has high accuracy/repeatability, but the method’s utility as a screening approach is constrained by low throughput and a complex workup procedure. In this work, a TGA curve-fitting method was developed to quantify the lignin content using the thermal decomposition profile of the unfractionated hardwood, softwood, and herbaceous biomass feedstocks. The method achieved comparable accuracy/repeatability to the NREL procedure with a significant reduction in the required characterization time, feedstock volume, and sample preprocessing prior to characterization. The TGA-derived thermal deconstruction profiles of the biomass were leveraged to predict both the theoretical maximum and experimentally determined lignin phenolic yields of native biomass for a reactive distillation - reductive catalytic fractionation process. In summary,
this method enables the direct prediction of LCB characteristics from whole biomass, thus increasing throughput and enabling facile biomass characterization.

Sulfo-functionalized lignin nanoparticle aerogel as a thermal insulator

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Residential heating and cooling accounts for the extensive use of thermal insulating materials to reduce their energy consumption. The current thermal insulating materials are derived from inorganic materials, or from petroleum-based materials, which pose both environmental concerns and hazards to human health. Thus, the need for a sustainable, green alternative material for thermal insulation is urgent. The present study attempts to utilize lignin, a low-cost biopolymer derived from lignocellulosic materials, with a proven capability to substitute petroleum-based polymers used in the production of thermal insulating aerogels.

The objective of the present study is to synthesize sulfoalkylated lignin nanoparticle (SLNP) that is able to improve homogeneity and dispersibility of lignin in aerogel systems improving the surface area and thermal insulation application of aerogels. This presentation discusses how the sulfo-alkylation reaction of lignin improved its characteristics as a biopolymer and nanoparticle formation as a main ingredient of aerogel fabrication. With the information gathered from advanced analysis, this presentation discusses how the properties of sulfo-alkylated lignin will impact its aerogel formation and performance as an insulating material.
Fast relaxing lignin-derived fully bio-based vitrimeric elastomers

Sargun Singh Rohewal1,2, srohewa1@vols.utk.edu, Nihal Kanbargi1, Amit K. Naskar1.
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Vitrimeric materials are an innovative polymeric material class comprising of covalently adaptive dynamic network stimulated by external factors, such as heat and UV light. Owing to the presence of dynamic exchangeable cross-link network, vitrimers feature thermoset-like mechanical and chemical resilience while also demonstrating flow on demand under external stimuli that are characteristic of thermoplastic-like materials. Currently, majority of the vitrimers reported utilize high Tg polymers which have long relaxation times (>100s), limiting their prospects for industrial-scale continuous processing techniques like extrusion and injection molding.

Herein, we synthesize a fast relaxing (characteristic relaxation time < 5s) fully biobased vitrimeric elastomer by utilizing a functionally enriched lignin oligomer and epoxidized natural rubber (ENR) in a solvent-free, high-shear reactive mixing process. Covalent interactions between the carboxyl group (from lignin) and oxirane (in epoxidized rubber) lead to formation of an ester based crosslinked network which undergoes topological rearrangement via transesterification exchange reactions (TERs) on thermal stimulation. The fast topological rearrangement induced by TERs at elevated temperatures is instrumental in enabling vitrimeric materials to be potentially useful for continuous (re)processing techniques, while also imparting sought-after properties like self-healing, shape recovery, and recyclability to the crosslinked matrix. Significantly, the lignin-based vitrimer demonstrated almost identical mechanical properties even after three reprocessing cycles. Additionally, incorporation of lignin with high elastic modulus in inherently soft
ENR matrix resulted in a material with high toughness and exceptional elastic recovery. Our approach and materials provide a promising pathway for circular and value-added utilization of lignin.

CELL 3917673

Lignin as a source of chemical feedstocks: boron trihalide mediated preparation of low-crosslinked lignin from white pine sawdust

Theodora E. Leventis1, theoleven05@gmail.com, Florence J. Williams1, MOHD ZAIN H. Kazmi2. (1) Chemistry, The University of Iowa, Iowa City, Iowa, United States; (2) Chemistry, University of Alberta, Edmonton, Alberta, Canada.

Lignocellulose is the structural component of all plant cell walls. As a result, lignin, cellulose, and hemicellulose are the most abundant biopolymers on the planet, and therefore an important resource for sustainable aromatic feedstock molecules (currently derived from petroleum sources). However, currently utilized methods of separating cellulose from lignocellulose degrades the lignin component, and the manner of that degradation frequently introduces new C–C linkages to the lignin structure that mitigates its depolymerization to access aromatic monomers.

The Williams Lab has discovered a method of using boron Lewis acids to cleave ether bonds mildly and selectively by using an equimolar mixture of boron tribromide and boron trichloride. This boron trihalide reaction was utilized to selectively separate the cellulose and hemicellulose components without subjecting the lignin sample to high temperatures, oxidants, or concentrated Brønsted acids, which facilitate crosslinking. Staining of the boron trihalide-treated sawdust sample with colorimetric dyes gave high confidence that the polysaccharide was efficiently extracted out, leaving a lignin-rich solid expected to possess a low level of crosslinking. This was further confirmed by solution and solid-state NMR spectroscopy, MALDI-MS, and IR spectroscopy.

This talk will describe the prior work developing the polysaccharide extraction method and will further explore characterization of the structural features of the lignin after extraction. These characterization investigations will provide insight into the mechanism of boron trihalide treatment of lignocellulose as well as measure the chemical value of remaining lignin.
CELL 3920321

Combating antibiotic resistance via lignin valorization

Shudipto K. Dishari, sdishari2@unl.edu. Chemical and Biomolecular Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, United States.

Antibiotic resistance is a severe public health concern on a global scale. This is the consequence of overuse and misuse of antibiotics as well as bacteria cleverly adapting themselves against the action of antibiotics. While the quest to design new antimicrobials are ongoing, an important fact to note here is that every year the United States spends about ~$50 billion to handle antibiotic resistance as per the Center for Disease Control and Prevention (CDC) report. Thus, if antimicrobials can be designed with low-cost, natural materials, we can effectively minimize the sky-high expense to manage antibiotic resistance, while supporting bioeconomy. This talk will present an affordable, scalable and highly efficient antimicrobial solution against antibiotic-resistant bacteria using inexpensive and biorenewable lignin. Lignin is a by-product of agricultural farms, pulp and paper industries and biorefineries. However, only ~2% of this lignin is currently valorized. We rendered cationic functionalities to alkali lignin so that the cationic lignin can interact non-specifically with charges on the cell envelope of antibiotic-resistant bacteria, a mechanism to which even notorious pathogenic bacteria find difficult to show resistance to. We demonstrated that treating both wild-type and kanamycin-resistant E. coli with cationic lignin can kill ~90% of the bacteria, and lead to ~100% growth inhibition. Our work also showed that this functionalized lignin can alter the lipid bilayer of bacteria and cause leakage of components from cell cytoplasm. Such cell envelope and internal damages of bacteria appeared to be the root cause of high antimicrobial efficacy of cationic lignin. Overall, this work demonstrated an efficient, affordable and sustainable antimicrobial solution using low-cost and abundant lignin and developed an informative framework on their antimicrobial action mechanism.

CELL 3922625

Understanding enzyme-solvent interactions to enable effective lignin valorization

Jian Shi, j.shi@uky.edu, Joseph Stevens, Can Liu. Biosystems and Agricultural Engineering, University of Kentucky, Lexington, Kentucky, United States.

Ionic liquids (ILs) have received increasing interest because of their high efficacy in fractionating and pretreating lignocellulosic biomass. Biocatalysis in a solvent system such as IL could improve the contact of the lignin polymer to the catalyst and the selective/controlled breakdown of inter-unit linkages. Prior results suggest different interactions and sensitivities of laccase enzyme to different ILs but do not provide enough explanation for these effects at a molecular level. We investigated the biocompatibility of IL with the laccases from various sources originated from plant, thermophilic fungus and hyperthermophilic bacterium. Surface charges of the laccase were modified via acetylation, succinylation, cationization, or neutralization toward improving activity and stability. Molecular simulations such as protein-ligan docking and molecular dynamics were car-
ried out to validate experiment studies and provide explanation on the observed enzyme-solvent interactions. This work demonstrates the use of a biocatalyst in a solvent system for in situ lignin valorization that can potentially improve the revenue stream of future cellulosic biorefineries.

**Intermission (20 min)**

**CELL 3929281**

**Insight into the depolymerization and demethylation of lignin under moderate conditions in the molten salt hydrate**

*Xuejun Pan*, xpan@wisc.edu. *University of Wisconsin-Madison, Madison, Wisconsin, United States.*

A molten salt hydrate (MSH) is a concentrated aqueous solution of an inorganic salt, in which the molar ratio of water to the salt is close to the coordination number of the salt cation. MSHs have many unique properties, such as low viscosity, high boiling point, low vapor pressure, and enhanced acidity, which make them distinctive and useful solvents for many chemical reactions. Some MSHs can swell and dissolve cellulose and therefore have been used as efficient solvents and reaction media for lignocellulosic biomass processing and conversion. Recently, it was found that a molten salt hydrate (lithium bromide trihydrate, ~61 wt% LiBr aqueous solution) can efficiently depolymerize lignin by cleaving β-O-4 linkage without causing condensation. Further studies revealed that other ether bonds of lignin in methoxyl, β-5, and β-β structures can also be cleaved in the LiBr system. This finding provided a new method for lignin demethylation. We found that kraft lignin was extensively depolymerized and demethylated in the LiBr system, and the depolymerized and demethylated kraft lignin showed excellent antioxidant activity and Cr(VI)-scavenging capacity, compared with original kraft lignin. In addition, lignin-derived aromatic compounds, such as 4-propylguaicol, 4-propylsyringol, 4-propanolguaicol, and 4-propanolsyingol were efficiently demethylated under mild conditions, leading to the corresponding catechol and pyrogallol derivatives in high yield.

**CELL 3920319**

**Lignin as a biopolymer for sustainable plastics development**

*Kavya Ganesan*¹², kavyag@clemson.edu, *James Sternberg*¹², *Srikanth Pilla*¹². (1) Automotive Engineering, Clemson University College of Engineering Computing and Applied Sciences, Clemson, South Carolina, United States; (2) Clemson Composites Center, Clemson University College of Engineering Computing and Applied Sciences, Greenville, South Carolina, United States; (3) Material Science and Engineering, Clemson University College of Engineering Computing and Applied Sciences, Clemson, South Carolina, United States.

Bisphenol-based epoxies are a class of high-performance polymer materials which when cured yield thermosets with high mechanical, thermal and chemical resistance properties. North America roughly produces around 123 billion pounds of these epoxies which
are used in a wide range of industrial applications like coatings, composites structural parts, automotive, electronics, construction etc. These epoxies are mainly manufactured from bisphenol-A and epichlorohydrin. Both these chemicals are acutely toxic and carcinogenic. During the life cycle of these different products in various applications, roughly around 1 million pound of BPA is released into the environment. The sustainability of epoxies would be enhanced by using a biobased material and prevention of usage of epichlorohydrin and bisphenol-A. Of available epichlorohydrin free biobased epoxies, the existing methods employ allyl bromide that is still acutely toxic and carcinogenic. Some vegetable oil-based epoxies do employ green methods to their synthesis. However, these epoxies are from non-aromatic source and hence have poor mechanical and thermal properties. In this work lignin from biomass is chosen as a suitable sustainable replacement for these toxic chemicals in manufacturing of bio-based epoxies through a non-toxic route. The use of lignin has the advantage of targeting high performance epoxy applications. Currently there exist no toxic free route to make epoxies from lignin without using epichlorohydrin or allyl bromide in the process. So, the scope of the work was developing epichlorohydrin free way of making epoxies from Kraft lignin. Vanillic acid was used as a model compound to develop and test the sustainable route using organic carbonates and peracids. Initial trials with model compound showed high rates of conversion enabling a path forward for Kraft lignin. Future work will study how to increase epoxy equivalent weight and create materials with similar mechanical and thermal properties as commercial epoxies.
Reactive extruded lignin in recyclable and biodegradable thermoplastic biomaterials

Angelica Avella\textsuperscript{1,2}, Marcus Ruda\textsuperscript{3}, Claudio Gioia\textsuperscript{4}, Valentina Sessini\textsuperscript{1,2,5}, Thomas Roulin\textsuperscript{2}, Christopher Carrick\textsuperscript{3}, Giada Lo Re\textsuperscript{1,2}, giadal@chalmers.se. (1) Department of Industrial and Materials Science, Chalmers tekniska hogskola AB, Goteborg, Sweden; (2) Wallenberg Wood Science Center, Goteborg, Sweden; (3) Lignin Industries AB, Knivsta, Sweden; (4) Department of Physics, Universita degli Studi di Trento, Trento, Trentino-Alto Adige, Italy; (5) Department of Organic and Inorganic Chemistry, Universidad de Alcalá, Alcalá de Henares, Comunidad de Madrid, Spain.

Lignin, abundant natural polymer, can be exploited for the fabrication of biomaterials to limit the consumption of fossil-based resources. This work proposes a circular design for the synthesis of recyclable and biodegradable materials based on technical lignin. In the first step, a bio-sourced epoxidized methyl ester was grafted onto non-purified and non-fractionated lignin via reactive extrusion, a sustainable scalable process, with the aim of lowering lignin glass transition temperature and improve its melt processability. Afterwards, the modified lignin was melt-blended with biodegradable poly(butylene adipate-co-terephthalate) (PBAT) to obtain biomaterials up to 80 wt.% lignin with tuneable thermomechanical properties. Lignin modification increased its interaction with PBAT and preserved the toughness of the biomaterials. Consequently, film blowing was carried out up to 40 wt.% modified lignin, as a conventional shaping technique for packaging and disposable products. Mechanical recycling and industrial composting were evaluated as feasible end-of-life options to assess the circularity of the blown films. The designed lab-scale approach was finally promoted to pilot-scale commercial production of biomaterials via one-step process in a twin-screw extruder.

Dynamic modeling of lignin-hemicellulose complex for maximizing monolignols production in organosolv pretreatment and depolymerization biorefinery system

Jianyu Guan\textsuperscript{1}, Ho Yin Tse\textsuperscript{2,1}, Shao-Yuan Leu\textsuperscript{1}, syleu@polyu.edu.hk. (1) Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, Hong Kong; (2) Yale University, New Haven, Connecticut, United States.

Monolignols are valuable products derived from lignocellulosic biomass, but its productivity is often limited by feedstock properties and treatment conditions in a biorefinery. To better control the process, accurate simulation is critical to quantify the dynamic status of lignin and hemicellulose removal in the lignin-hemicellulose complex. Hence, this study investigated the relationships of a few essential parameters such as the pretreatment factors, lignin removal, $\beta$-O-4 linkages, and monomer yields based on the results of 62 biorefinery experiments. A novel structural model was developed to successfully simulate (90.88% Accuracy) the performance of biomass separation and lignin condensation (-OH function group and $\beta$-O-4 linkages) over changing temperatures, time, and acid
catalyst concentrations. The mechanism of lignin condensation was revealed upon the loss of hydroxyl groups at C9&C7 positions, which numerically described the lignin reprecipitation in acid-catalyzed organosolv. Further, the dissolved lignin was subjected to catalytic transfer hydrogenolysis to produce monolignols. The monomer yield was compared with other techniques based on various delignification principles, with identification of changing lignocellulosic structure via 2D HSQC NMR spectroscopy and chemical composition analyses. The implementation of the new model was applied in the establishment of a continuous flow reactor system which increased the monomer yield by 30%; while achieving a lignin separation efficiency of more than 95%. The model has shown its potential in process control and optimization especially for urban biorefinery with high variety of lignocellulosic biomass derived from municipal wastes.


Symposium Separates

CELL 006
“Inaugural ACS CELL Division Symposium on Industrial Renewable Materials”

Organizers
Stoyanov, Edmont, Technical Director, Nisso Chemical Europe GmbH; Larkin, Glenn, LarChem LLC; Jiang, Feng, The University of British Columbia; Elkins, Casey, Eastman Chemical Co; Vignolini, Silvia, Cambridge University; Lucia, Lucian, North Carolina State University.

Symposium CELL 006A (Hybrid)
Sunday 8/13/2023 morning – Moscone Convention Center, Room 302, South Bldg.

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CELL 3927650

Eastman Aventa™ compostable products: biobased with recycle content

Jos S. de Wit, Casey Elkins, clelkins@gmail.com. Eastman Chemical Co, Kingsport, Tennessee, United States.

The value of Eastman Aventa™ Renew compostable products can be discussed in three distinct stages: the beginning of life (BOL), in use performance, and end of life (EOL). This presentation will use Aventa™ FT1200, the first commercially available compostable product in use to manufacture drinking straws, to discuss all three aspects that enable a truly circular economy.

This presentation focuses on the beginning of life, specifically the renewable content, consisting of bio content and recycle content. This formulated product consists of cellulose, glycerol, and acetyl and is nearly 100% renewable. The various ways of calculating renewable content, including biocarbon, will be shown.

The performance of the product has two distinct aspects, namely the ease of use by the converter, making the Aventa™ pellets into straws, and the consumer experience. In both cases Aventa™ was directly compared with the familiar polypropylene straws. The end of life, which is the reason behind the entire program, should be composting.
Straws made from Eastman Aventa™ FT1200 are certified for industrial composting and home composting. The impact of compost on global warming and quality of soil to grow our food cannot be overstated. Someone noted that our ability to live depends on 6 inches of good topsoil and the fact that it rains every now and then. Aventa™ FT1200 is not only renewable itself, but through diversion of food waste from the landfill to the composter reduces methane emissions and also renews our soil.

**CELL 3891351**

**Bio-stimulants from sugarcane processing byproducts**

**Sophie M. Uchimiya¹, sophie.uchimiya@usda.gov, Anthony Hay². (1) USDA-ARS Southern Regional Research Center, New Orleans, Louisiana, United States; (2) Cornell University, Ithaca, New York, United States.**

Raw sugar production involves high temperature sedimentation processes to remove impurities. The sedimentation byproduct (often called mill/press mud) is pasteurized and contains added phosphorus to facilitate the sedimentation of organic carbon. While mined phosphorus reserves are projected run out in the coming decades, recent geopolitical events have highlighted the immediate need to reclaim phosphorous used by industry as sources of fertilizer. This presentation will describe historical handling of sugarcane mill mud and emerging/potential industrial applications. Although it is pasteurized at elevated temperature, mill mud still retains organisms and functions that could enhance soil microbial diversity, increase disease resistance and improve crop health. To commercialize mill mud as a bio-stimulant, the sugar industry needs the technical interface for customers seeking alternative fertilizers to grow crops. Specialized finished products like biostimulants may require advanced data to show the functional capacities of sugarcane mill mud over chemical fertilizers or commercial composts. This study utilized bioinformatics and cheminformatics approaches that could be adapted by the sugar industry for commercialization of mill mud as biofertilizer with benefits for crop and soil health.

**CELL 3920049**

**Application of structural colour towards improving the sustainability of white printing inks**

**Andrew Kyriacou¹-², ak2325@cam.ac.uk, Yating Zhang¹, Silvia Vignolini¹, Lukas Schertel¹, Josie Harries². (1) University of Cambridge, Cambridge, United Kingdom; (2) Domino Printing Sciences plc, Cambridge, Cambridgeshire, United Kingdom.**

Inkjet inks are used by companies worldwide to print on their products before being sold to end users, and it is expected that the inks and coatings industry will produce 3.6 million tonnes in 2023. Due to the vast volumes of inks being printed every year, increasing focus has been turned towards improving their environmental impact. For white inks, the colourant traditionally used is titanium dioxide pigment due to its high opacity and ease of formulation. However, the recent concerns of the effect of titanium dioxide on human
health and its energy intensive dispersion process stimulated the field to finding new approaches to develop white colouration.

Here we present formulations based on cellulose derivatives capable of producing bright white colours. In our work, the whiteness is the result of light interaction with highly scattering, porous cellulosic films obtained via evaporation induced phase separation. We demonstrated that these white films can be constructed by depositing a clear, colourless, and homogeneous cellulosic formulation with a continuous inkjet printer. After evaporation of the solvents, the measured reflectance is higher than titanium dioxide-based formulations of equal solids content. Moreover, we showed that by incorporating a suitable co-binder, the abrasion resistance of the printed inks can be improved while simultaneously maintaining the white colour. The developed strategy therefore represents a scalable and industrially relevant approach for the application of structural colour in the inkjet industry.

CELL 3922885

**Development of biomass-modified bamboo fibers for reinforcing asphalt-based composites**

Renhui Qiu, renhuiqiu@fafu.edu.cn, Wendi Liu, Xiaoyan Zheng. College of Transportation and Civil Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian, China.

Bamboo fiber (BF) has attracted much attention for asphalt pavements due to its high strength, low-cost, renewability, and biodegradability. However, one critical factor limiting the application of BFs in asphalt-based composite is the weak fiber-matrix adhesion. Therefore, this study proposes a surface modification method of BFs using acrylated epoxidized soybean oil (AESO) and 4,4-methylene diphenyl diisocyanate (MDI) to improve the fiber-matrix adhesion. The surface chemistry of the BFs was characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance. Moreover, the fiber-matrix adhesion was evaluated using water-boiling test and scanning electronic microscopy, and the enhancement mechanism was investigated. The results showed that the BF surface was grafted with AESO via a linkage of MDI, forming a chemical connection with the asphalt matrix. Thus, the interfacial adhesion between the modified BFs and asphalt matrix was remarkably enhanced, significantly improving the road performance of the asphalt-based composites.

*Intermission (20 min)*
Perspectives on academia-industry research collaborations in bioproducts

Scott Renneckar, scott.renneckar@ubc.ca. Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada.

Academic research can have the stigma of disconnected science far removed from relevance for society. Even if applications or technology can be developed for commercial opportunity, there is the 'valley of death' where innovations are not scaled beyond the bench. However, the synergy between academia and industry is critical to help develop both impactful and feasible technologies and offer additional training to graduate students. As a principle investigator that has research in the applied science area of bioproducts, such as lignin and renewable materials, having industry participate either actively or passively in research has been extremely helpful to understand better how to have impact with the research outputs. Over the years, our group has worked with industry consortia on pre-competitive research on topics relative to a specific industry, as well as research partnerships that leverage federal funding. This talk will provide the perspective from the principle investigator’s point of view for a recipe for success, the hiccups that can be involved with working in academia, and an overview of some collaborative Canadian grant opportunities.

Addressing the plastic waste crisis by moving toward a circular economy

Katherine Hofmann, kahofmann@eastman.com, Dayton Street, Holli Alexander, Casey Elkins, clelkins@gmail.com. Eastman Chemical Co, Kingsport, Tennessee, United States.

Plastic materials are utilized in diverse markets and are ubiquitous in industrial and household products. For example, plastics are commonly used to hydrate (drinkware), feed (food storage, packaging), and care (medical accessories) for the growing global population. While plastics in these applications highlight their importance in improving the quality of life, recent focus has shifted to end-of-life implications. In this session, I will discuss the plastic waste issue and how Eastman is utilizing chemical recycling technologies to move towards a more circular economy.

Lignin-derived carbon aerogels for energy storage and CO2 capture applications: Crosslinking and surface activation for tunable pore structure and enhanced properties

Muzaffer Karaaslan¹, muzaffer.karaaslan@ubc.ca, Li-Ting Lin², Frank K. Ko², Scott Renneckar¹. (1) Advanced Renewable Materials Laboratory, Department of Wood Sci-
In recent years, the increasing concerns over greenhouse gas emissions and their impact on global climate change have led to a growing demand for sustainable materials with high-performance properties for energy storage and CO$_2$ capture applications. Carbon aerogels are promising materials for these applications due to their tunable three-dimensional hierarchical network structure, high specific surface area, and mesoporosity. Furthermore, the development of sustainable production methods for carbon aerogels using renewable resources has attracted significant attention. Lignin, a renewable aromatic biopolymer with high carbon content and chemical functionality for crosslinking, offers a promising alternative to traditional non-renewable and toxic phenolic precursors for the production of carbon aerogels.

In this study, we prepared carbon aerogels using industrial softwood kraft lignin with different crosslinking methods and investigated the effects of crosslinker type and surface activation on the pore structure and resulting properties. We examined the effect of lignin-to-crosslinker ratio and lignin content on the chemical and physical properties of carbon aerogels, including their density, surface area, and pore size distribution. Moreover, we evaluated the effect of chemical surface activation on the specific surface area, microstructure, and porosity of aerogels using N$_2$ and CO$_2$ gas adsorption.

Our results showed that the activated lignin carbon aerogels exhibit superior electrochemical capacitance compared to commercial resorcinol-formaldehyde-based carbon aerogels and activated carbon, making them promising candidates for energy storage applications, such as supercapacitors. We also evaluated the CO$_2$ adsorption capacity of lignin carbon aerogels and found that sub-nanometer porosity significantly enhanced their capacity at 100 kPa, indicating their potential as effective adsorbents for CO$_2$ capture applications.

Overall, our findings highlight the importance of crosslinking method and surface activation for tuning the pore structure and properties of carbon aerogels and demonstrate the potential of lignin-based carbon aerogels for sustainable, high-performance energy and environmental applications.
Sustainable advanced Fenton-like catalysts based on mussel-inspired magnetic cellulose nanocomposites to effectively remove organic dyes and antibiotics

Guihua Wang, wangguihuascu@163.com, Jun Xiang, Sheng Chen, Bin Yan, Haojun Fan. National Engineering Laboratory for Clean Technology of Leather Manufacture, College of Biomass Science and Engineering, Sichuan University, Chengdu, Sichuan, China.

As an emerging class of biocompatible plant-derived nanomaterials, cellulose has attracted great attention in applications of wastewater treatment because of its natural abundance, environmental friendliness, and high strength. However, it remains a great challenge to develop biocompatible advanced Fenton-like catalysts with high catalytic
activity, good stability and recyclability using cellulose. Herein, we develop a novel mussel-inspired magnetic cellulose nanocomposite (MCNF/PDA) with carboxylated cellulose nanofibers (CNF) and explore as advanced Fenton-like catalysts to effectively degrade organic dyes and antibiotics. The composites exhibit an excellent degradation activity towards methylene blue (MB) in a wide pH range of 2-10 in presence of H₂O₂ and have a maximum degradation capacity of 2265 mg/g. In particular, at pH 10, it can reach a very high degradation rate of 0.342 min⁻¹, which is 20 times that at pH 2. Moreover, the MCNF/PDA catalyst can be easily separated and highly recyclable. After four consecutive runs, the removal rate can still keep more than 95%, indicating that the polydopamine layer can protect Fe₃O₄ from iron loss and increase its stability. Meanwhile, the catalysts exhibited a similar degradation performance effect to the antibiotic tetracycline. This work provides new insights into fabricating biocompatible cellulosic nanomaterials with biomass derived materials as advanced Fenton catalyst for efficiently removing organic pollutants from wastewater.

**CELL 3913667**

**Plant-inspired design of sandwich-like hierarchical leather with unidirectional water transportation for efficient moisture management**

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With climate warming in full swing, heat-resulted physiological and psychological discomfort threatens human health and excessive sweat secreted from the skin often causes sticky and uncomfortable feelings in outdoor conditions. Leather as a kind of in-
termediary between the skin and the condition, plays important roles in achieving personal moisture and management that focuses on the drying of localized human bodies. However, it slowly evaporates sweat due to uniform treatments, and partial sweat retention on the skin side. Moisture-managing materials with modified wettability or fiber structures to enhance sweat wicking and evaporation are emerging as a promising solution to settle personal comfort without large-area space cooling/heating. Inspired by the strong water transportation of plants due to its hierarchically porous structure, a sandwich-like hierarchical leather with both surface energy and aperture gradient was developed (denoted as SDGL). The incorporated polymer networks with different wettability and aperture on the opposite sides of the leather established reliable surface energy and the aperture gradient. Benefiting from this sandwich structure, SDGL exhibited unidirectional water transportation and antigravity rise in pH range of 4.5~9. When a water droplet contacted the bottom hydrophobic side with large pore, it was directly pumped upward into the upper hydrophilic side. However, when the hydrophilic side with small pore faced up, the water only spreads along without penetrating through the leather. A practical outdoor test demonstrated that the SDGL can weaken the sticky adhesion, promote sweat removal, and avoid excessive cool feeling on the skin (1.5~2 °C higher than with cotton). Moreover, due to abundant porous in SDGL structure, it possessed excellent breathability (>2500 mL/cm²·h) and moisture permeability (>350 mg/cm²·24h). This work is valuable for industrial and outdoor workers and provides new inspiration for the design of advanced functional leather to provide personal comfort in outdoor conditions.

CELL 3914119

Study on the construction of bone defect barrier membrane with immune homeostasis regulation ability and heterogeneous bilayer structure based on collagen

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Alveolar bone defect is the main obstacle of dental implantation. The current solution is placing a barrier membrane between the soft tissue and bone defect area to induce bone regeneration based on guided bone regeneration. However, the current barrier membrane has different degrees of defects. This study aims to construct a barrier membrane with immune homeostasis regulation ability and a heterogeneous bilayer structure based on collagen. The compact surface layer can block the connective tissue that hinders bone regeneration, and the porous bottom layer can provide three-dimensional space for osteoblasts to grow. Immunomodulatory drugs encapsulated in nanocarriers can confer immune homeostasis regulation properties on barrier membranes. Collagen was crosslinked by dialdehyde carboxymethyl cellulose to prepare the membrane. Monolayer membranes with different pore sizes were constructed by adjusting the degree of crosslinking and the long/short range of crosslinking reaction. Two membranes were compounded by self-healing properties to realize the heterogeneous bilayer structure. We have studied the physicochemical properties and biological properties of the membrane, focus on the variation of pore size and viscoelasticity and the regulation methods of the membrane, explore the pore size and viscoelasticity specificity for fibroblasts and osteoblasts growing, and reveal the optimal regulation mechanism of the heterogeneous
double-layer structure of the barrier membrane. The results have provided a new idea for the design and preparation of the new high-performance bone defect barrier membrane.

**CELL 3914852**

**Room temperature dissolution of cellulose with a metal salt hydrate-based deep eutectic solvent**

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Cellulose, the most abundant natural polysaccharide is considered an almost inexhaustible resource, is one of the most promising substitutes of petroleum-derived synthesis polymers. Nevertheless, cellulose with numerous hydroxyl groups and electronegative atoms can form extensive hydrogen bonds, which are non-negligible obstacles to its dissolution and further utilization. Herein, to realize the room temperature dissolution of cellulose with an inexpensive and eco-friendly solvent, we design a novel metal salt hydrate-based deep eutectic solvent that functions as molecular scissors to break the strong hydrogen bonding networks within cellulose. Various types of cellulose (e.g., microcrystalline cellulose, wood cellulose, pulp cellulose, cotton linter) can be spontaneously and efficiently dissolved, and the advantages of open system, convenient operation, excellent dissolution efficiency, easy scaling up, good recyclability for this solvent were experimentally demonstrated. The diverse regenerated materials of cellulose (e.g., hydrogels, films, and silk materials) are constructed via an anti-solvent induction method. Therefore, the studies will boost the fundamental research and industrial manufacturing of cellulose resource.

**CELL 3915229**

**Production of biomass-based composite from reed pretreated by ball-milling combined with p-toluenesulfonic acid**

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Reed is a promising biorenewable energy source given its ability to grow rapidly under environmentally challenging conditions. Pretreatment of reed by ball-milling in the presence of p-toluenesulfonic acid (p-TsOH) led to a significant reduction in hemicellulose (78%) and lignin (67%) content. After this pre-treatment, enzymatic hydrolysis of the residue led to a glucose content of 12.0 g/L. The enzymatic hydrolysis showed improved performance when ball-milling was included in the pre-treatment process. Both the residual lignin (extracted after pretreatment) and the solid residue (post enzymatic hydrolysis) were blended with polylactic acid (PLA) to prepare bio-based composites by injection molding, with the latter residue-plastic composite (RPC) possessing better mechanical properties. The bending strength, Young's modulus, bending modulus and impact
strength of RPC were 29.08 MPa, 582.7 MPa, 879.4 MPa and 13.44 KJ/m², respectively. The melting and crystallization temperatures of the composite were lower than that of pure PLA.

**CELL 3919865**

**Molecularly engineered cellulose hydrogel electrolyte for highly stable zinc ion hybrid capacitors**

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Aqueous zinc ion hybrid capacitors (ZIHCs) are considered as one of the most promising prospects to incorporate the merits of supercapacitors and batteries as well as inexpensive, extremely safe, and eco-friendly, displaying a great promise in industrial production. Unfortunately, the infamous Zn dendrite growth and the parasitic side-reactions seriously hamper their cycling stability and Zn plating/stripping coulombic efficiency. Herein, we proposed a sustainable molecular engineering strategy to regulate zinc electro-deposition behavior by designing a carboxylic acid functionalized cellulose (COOH-Cell) hydrogel electrolyte in the newly developed solvent system of super-base/DMSO/CO₂. We discovered that the solubilization and derivatization of cellulose expanded the inherent inter-/intra hydrogen bonds network, resulting in the formation of unblocking the ion channels. Impressively, carboxylic acid functional groups achieve the homogeneity of the zinc electrodeposition process and induce the formation of quasi-SEI layers, which effectively inhibits zinc dendrites. Consequently, the cycle stability of the zinc plating/stripping in Zn||Zn cell exceeds 2000 h at 1 mA cm⁻². The ZIHCs deliver a superb cycling life of 70,000 cycles with 91 % capacity retention at 5 A g⁻¹. This strategy proposed here opens up a fresh route for cellulose hydrogel electrolytes to regulate the deposition behavior of Zn for high-performance zinc-based energy storage systems.

**CELL 3915895**

**Regulation of cellulose nanocrystals-based dynamic schemochrome for functional applications**

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As an abundant and renewable biomass resource, the rod-like crystalline cellulose nanocrystal (CNC) has gained extensive interest due to its high specific strength, high specific surface area, biocompatibility and especially unique photonic properties. Evaporation-induced self-assembled CNC suspension can form an iridescent cholesteric liquid crystal (LC) nanostructure, which can selectively reflect particular wavelength of incident light and display variable structural color. Unfortunately, the assembly process and the resulted LC structure are hard to control, which severely restrict the uniformity and saturation of the structural color. Besides, the pure CNC with non-adjustable helical pitch is quite fragile and only has static optical properties, so that the application of CNC in intel-
ligent optical systems is limited. To address the above problems, we focus on the regulation of self-assembled CNC nanostructure, and carry out a series of work about functionalization of the related dynamic schemochrome. Based on the design of hybrid co-assembly system and introduction of multiple particle–interface interactions, uniform LC structure with adjustable structural color is tightly combined with flexible polymer, whether on the surface or inside the matrix. In addition, by incorporating stimulus-responsive component, dynamically correlations are established between adjustable helical pitch and external stimulus including force, humidity, infrared light and heat, which further enable wide-range adjustable optical characteristic and identifiable visualized patterning. The developed series of materials are separately applied in proof-of-concept demonstrations of several intelligent devices with synergistic dynamic schemochrome, including multi-stimuli responsive actuating, self-healable wide-range strain-sensing and dual-responsive encryption patterning. We envisage that the novel strategy for constructing CNC-based material with dynamic structural colors will hold promise in the design of next generation intelligent optical devices and may find applications in smart soft display, anti-counterfeiting, wearable optical devices and intelligent control systems.

CELL 3916424

CO$_2$-fueled nonequilibrium catalytic polymerization in transient breathing nanogels

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Gas whether can be harnessed as a chemical fuel to drive dissipative process remains challenging. Here we present a “breathing” nanogel that is fueled by CO$_2$ gas to perform temporally programmable catalytic polymerization. The nanogel is composed of unique frustrated Lewis pair polymers (FLPs). By forming dynamic CO$_2$-FLP gas-bridging bonds, addition of CO$_2$ endows the nanogel with a transient volume contraction, and the resulting proximal effect of activated FLP units unlocks its catalytic capacity toward CO$_2$. Subsequent depletion of the gas fuel through a CO$_2$-participated polymerization can induce a reverse nanogel expansion of nanogel, which shuts down the catalytic activity of FLPs. This nonequilibrium breathing behavior could be maintained as long as CO$_2$ is supplied. Moreover, control of external parameters (fuel level, temperature or competing additives) can regulate the breathing period, amplitude and lifetime, so as to affect the polymerization kinetics. Editing the breathing procedure of nanogel can sequentially evoke the copolymerization of CO$_2$ with different loaded epoxide monomers, thus obtaining block-tunable copolycarbonates that are hard to achieve by other ways. This dissipative synthetic system would be function as a prototype of gas-driven nanosynthesizer.
Preparation of full lignin-based adsorbent for the removal of heavy metal ions and its application in wound care dressing

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Recently, the application of lignin activation by demethylation to improve reactivity and enrich multiple functions has intensively attracted attention. Herein, an effective demethylation way was explored by microwave-assisted method for substantially enhancing the hydroxyl (-OH) content and retaining the structure of lignin. Then, the optimum demethylated lignin was used to removal heavy metal ions and promote wound healing, respectively. In detail, for microwave-assisted demethylated poplar lignin (M-DPOL), the contents of phenolic (Ar-OH) and total hydroxyl (Tot-OH) groups reached the maximum for 60 min at 90\degree C in DMF with 7.38 and 9.13 mmol/g, respectively. Subsequently, the maximum adsorption capacity (Q_{\text{max}}) for Pb\textsuperscript{2+} ions reached 104.16 mg/g using the M-DPOL as lignin-based adsorbent. Based on the isotherm, kinetic and thermodynamic models analyses, the chemisorption occurred in monolayer on the surface of M-DPOL, and all adsorption processes were endothermic and spontaneous. Meanwhile, M-DPOL as a wound dressing had good antioxidant property, excellent protein adsorption capacity, outstanding bactericidal activity and remarkable biocompatibility, suggesting that it did not interfere with cell proliferation. Especially, the in vivo test results showed that the wounded rats treated with M-DPOL significantly promoted the formation of re-epithelialization and wound healing of full-thickness skin defects. Overall, the microwave-assisted demethylated lignin not only has the excellent adsorption capacity of heavy metal ions, but also offers great advantage for wound care dressing, which accelerates the high-value utilization of lignin.
Active center reconstruction is essential for high performance oxygen reduction reaction (ORR) electrocatalysts. Usually, the ORR activity stems from the electronic environment of active sites by charge redistribution. We introduce an asymmetry strategy to adjust the charge distribution of active centers by designing conjugated polymer (CP) catalysts.
with different degrees of asymmetry. We synthesized asymmetric backbone CP (asy-PB) by modifying B←N coordination bonds and asymmetric sidechain CP (asy-PBA) with different alkyl chain lengths. Both CPs with backbone and sidechain asymmetry exhibit superior ORR performance to their symmetric counterparts (sy-P and sy-PB). The asy-PB with greater asymmetry shows higher catalytic activity than asy-PB-A with relatively smaller asymmetry. DFT calculations reveal that the increased dipole moment and non-uniform charge distribution caused by asymmetric structure endows the center carbon atom of bipyridine with efficient catalytic activity.

CELL 3916699

Tannery solid wastes-derived amphiphilic composite fibers for dual separation of oil-in-water and water-in-oil emulsions

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Animal skins derived from domestic animals such as pigs, cattle and sheep are important renewable animal biomass resources in nature. The main industrial application of animal skins is leather-making. However, a large quantity of tannery solid wastes (TSWs) is generated during the leather manufacture process. To address this concerned issue, the resource utilization of TSWs seems like an efficient way to tackle tannery pol- lutions and promote sustainable green development of leather industry. TSWs are mainly comprised of amphiphilic collagen fibers with unique regional infiltration. The hydrophilic and hydrophobic region contained in TSWs are able to selectively infiltrate the water and oil phases, thus showing great merits for the separation of both oil-in-water (O/W) and water-in-oil (W/O) emulsions. In addition, TSWs retain the hierarchically fibrous structure of collagen fibers from nanoscale to microscale, which exhibit excellent capillary effect to facilitate the rapid liquid transport along the fiber direction. Therefore, TSWs are also expected to enhance the mass transfer kinetics during the emulsion separation. Here, we developed a brand-new TSWs-derived amphiphilic composite fiber through in-situ growth of metal-organic-frameworks (MOFs) with excellent size-sieving effect on the surface of TSWs, followed by the decoration with amphiphilic BT-Cu^{2+} complexes formed by the coordination of bayberry tannin (BT) and copper ions (Cu^{2+}). The TSWs-derived amphiphilic composite fibers successfully realized dual separation of O/W and W/O emulsions by the synergy existed between the size-sieving demulsifying capability of MOFs and the demulsifying capability derived from the regional infiltration of TSWs decorated with amphiphilic BT-Cu^{2+} complexes. The separation efficiency was as high as 99.9989% and flux high up to 2891.7 L m^{-2} h^{-1}. Notably, the TSWs-derived amphiphilic composite fibers also displayed appreciable anti-fouling performance and reus- ability. Our investigation developed new technical approaches for the high-value re- source utilization of TSWs, which also provided efficient solutions for treating the emulsion wastewater.
**CELL 3916826**

**Tannin foam immobilized with ferric ions for efficient removal of ciprofloxacin at low concentrations**

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The presence of ciprofloxacin (CIP) in natural water may cause potential threats to the environment. In the environment, CIP is frequently detected for its high mobility. CIP has poor biodegradability, and its persistence in the environment may cause adverse effects to the microbial communities, imposing great risk to the non-target species in the ecosystems. Adsorption is a convenient and efficient method to remove CIP from aqueous solution. Bayberry tannin (BT), a natural polyphenol, has been utilized in the synthesis of tannin foam (TF) due to its abundant polyphenolic hydroxyls to chelate with metal ions. The obtained TF was subsequently immobilized with Fe³⁺ via a facile chelative adsorption to fabricate functional tannin foam (TF-Fe). TF has spherical microstructure with stacked voids formed among the spheres. The microspheres have the diameter of 2.0–4.0 µm and their rough surfaces are composed of subunit nanoparticles. The Fe species in the TF-Fe featured good dispersity, which were active for chelative adsorption of CIP. The adsorption of CIP on the TF-Fe was a pH-dependent process. When applied in removal of CIP at the low concentration of 2.0 mg L⁻¹, a high removal efficiency of TF was still obtained, which was superior to commercial activated carbon. The adsorption kinetics were well fitted by the pseudo-second-order rate model while the adsorption isotherms were well described by the Langmuir model. The adsorption of CIP on TF-Fe was demonstrated to be an endothermic process, which was closely related to the coordination of immobilized Fe ions with CIP. The TF-Fe was capable of recycling, which still maintained a high removal efficiency in the 5th cycle. The composite foam developed here may provide a promising approach for resolving the contamination of ciprofloxacin antibiotics in aqueous solutions.

**CELL 3916777**

**Biomimetic bridging for reconstructing biomass components toward significantly enhanced films from the full composition of bamboo**

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Bamboo is a kind of renewable natural polymer resource. Using bamboo biomass without a component isolation process can be a sustainable route for the preparation of an eco-friendly biomass film. Inspired by the natural structure of plant biomass, we designed to introduce a bionic interaction, being akin to the role of hemicellulose in natural biomass, for connecting the cellulose and lignin components using tannic acid-modified cellulose nanocrystals (TA@CNCs) as the bridging molecules. In order to make up for the size difference between the cellulosic molecules and lignin particles, cellulose nanocrystals (CNCs) served as the carriers of TA. Core–shell hybrids of TA@CNCs were
prepared and added into the solution of bamboo powder dissolved in a tetrabutylammonium hydroxide/dimethyl sulfoxide aqueous solvent (TBAH/H₂O/DMSO) followed by gelation in air and regeneration in water to prepare the bamboo-derived biomass films with high strength. The results showed that the tensile strength of the as-prepared films was effectively improved from 55.4 to 127.2 MPa by adding 5 wt % TA@CNCs. Structural analyses indicated that TA@CNCs serve as an excellent modifier for the enhancement of cellulose–lignin interfaces by rationally reconstructing the biomimetic hydrogen-bonded system.

CELL 3918699

Wood aerogel-derived sandwich-like layered nanoelectrodes for alkaline overall seawater electrosplitting

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Facile and controllable fabrication of eminently active and durable bifunctional catalysts for seawater electrolysis is significant for hydrogen production due to the shortage of freshwater resources. However, its implementation remains as a major challenge since the anodic reaction is sluggish. Here, we designed an artificial sandwich-like S,P-(Ni,Mo,Fe)OOH/NiMoP/wood aerogel electrocatalyst for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The sample required low overpotentials of 297 mV for OER and 258 mV for HER to achieve 500 mA cm⁻² in alkaline seawater. The features of the 3D wood aerogel, including open and well-aligned microchannels, large specific surface area, and good wetting ability, endow the as-synthesized electrocatalysts with impressive OER and HER activities. The two-electrode electrolyzer provides 500 mA cm⁻² at 1.861 V for overall seawater electrolysis. This work opens new avenues for developing effective and robust OER/HER catalysts for seawater electrolysis, which significantly advances clean energy systems research.
Bayberry tannin modified chitosan fibers for selective adsorption and removal of Cu(II) from aqueous solutions at low concentrations

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Selective adsorption removal of copper ions from aqueous solutions with low concentration is highly desirable because it allows easy separation and is of primary importance for a clean environment and human health. In this study, bayberry tannin modified chitosan microfibers (BT-CM) were synthesized for the removal of Cu\textsuperscript{2+} from aqueous solutions via glutaraldehyde cross-linking grafting method. Scanning electron microscopy (SEM) showed that the as-prepared BT-CM had well-defined microfiber morphologies. Its adsorption toward Cu\textsuperscript{2+} was found to be dependent on pH, adsorbent dosage and contact time. In batch experiments, the adsorption capacity of BT-CM to Cu\textsuperscript{2+} was up to 14.98 mg/g at 303 K in the range of pH 5.0; the adsorption capacity was higher than that of most conventional adsorbents and activated carbon. Equilibrium data for Cu\textsuperscript{2+} adsorption were well fitted with the Langmuir model and Freundlich model, and the adsorption kinetics of Cu\textsuperscript{2+} followed a pseudo-second-order model. The Cu\textsuperscript{2+} adsorbed on BT-CM can be desorbed by diluted acid solution with 96.6% desorption efficiency and the BT-CM exhibited good recyclability. Furthermore, evaluating the selective adsorption of Cu\textsuperscript{2+} by BT-CM within the co-existing cations, such as Ni\textsuperscript{2+}, Cd\textsuperscript{2+}, Fe\textsuperscript{3+} and Cr\textsuperscript{3+}, appeared...
that these co-existing ions had no critical impact on the adsorption of Cu\(^{2+}\), indicating the high selectivity for removal of Cu\(^{2+}\) at low concentrations from aqueous solutions.

CELL 3907505

Hydrodeoxygenation of guaiacol to phenol using endogenous hydrogen induced by chemo-splitting of water over a versatile nano-porous Ni catalyst

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In this work, an innovative route for upgrading biomass-derived phenolic monomers by "hydrogen-free" hydrodeoxygenation (HDO) was proposed and evaluated. The HDO process was integrated with the activation of water and aqueous phase reforming of in-situ generated methanol over a nano-porous Ni catalyst and finally established the one-pot approach achieving high selectivity of bio-phenol. DFT calculation confirmed the crucial role of Ni catalyst in the activation of water and following HDO process. The study on reaction pathway and mechanism showed that the initial hydrogen source came from water splitting on the surface of the Ni catalyst, which triggered the fracture of aromatic ether bond to afford phenol and methanol. The subsequent aqueous phase reforming of methanol generated more hydrogen and further accelerated the HDO process. Under optimized condition the conversion of guaiacol reached 41.5% and selectivity of phenol can be 100% at 160 °C. Further improve the temperature to 190 °C, a high conversion of 96.3% could be achieved while maintaining the selectivity of phenol to 77.9%. After a smart design of releasing methanol during reaction, the conversion and selectivity could be further improved to 90.5% and 90.3% respectively. Overall, the proposed method demonstrates the feasibility of upgrading oxygen-containing biological compounds in neat water system integrated chemo-splitting of water with using endogenous hydrogen for self-hydrolysis inhibiting external hydrogen supply.

CELL 3915144

Orientated inhibition of humin formation in efficient production of levulinic acid from cellulose with high substrate loading: Synergistic role of additives

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The main bottleneck in the direct conversion of cellulose to levulinic acid (LA), a promising bio-based platform chemical, lies in the severe formation of humins, especially at high substrate loading (>10 wt.%). Herein, we report an efficient catalytic system consisting of a 2-methyltetrahydrofuran/water (MTHF/H\(_2\)O) biphasic solvent with NaCl and
Cetyltrimethylammonium bromide (CTAB) as additives for converting cellulose (15 wt%) to LA in the presence of a benzenesulfonic acid catalyst. We show that both NaCl and CTAB accelerated the depolymerization of cellulose and formation of LA. However, NaCl favored the humin formation via degradative condensations, whereas CTAB inhibited humin formation by restraining the routes of both degradative and dehydrated condensations. A synergistic role of NaCl and CTAB on suppressing humin formations is illustrated. The combined use of NaCl and CTAB led to an increased LA yield (60.8 mol%) from microcrystalline cellulose in MTHF/H2O (VMTHF/VH2O = 2/1) at 453 K for 2 h. Moreover, it was efficient for converting cellulose fractioned from several kinds of lignocellulosic biomass, wherein a high LA yield of 81.0 mol% was achieved from wheat straw cellulose. This work presents a new strategy for advancing LA biorefinery by synergistically promoting cellulose depolymerization with orientated inhibition of undesired humin formation.

**CELL 3912705**

**Highly ordered regenerated cellulose films for electrostatic energy storage**

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Polymer-based dielectrics, ascribed to their brilliant flexibility and easy processing, have been extensively explored in applications for electronics and electric power devices. However, fabricating the full organic polymer dielectrics through a feasible way without introducing any other components is still a long-standing challenge, especially for the polymers produced from the natural resources. We demonstrate that substrate exhibits great role in tailoring the microstructures of dielectrics. The polar substrate promotes the highly ordered stacking of cellulose macromolecules, enhancing the intermolecular interaction and reducing or even eliminating defects. We fabricate a biodegradable cellulose film with energy density of 10.39 J/cm³ and efficiency exceeding 93%, and high energy density of 5.66 J/cm³ at 120 °C. Deterministic control of macromolecular alignment by substrate-dielectric interaction opens a novel path for high performance polymer-based dielectrics industries.

**CELL 3917888**

**Cellulose fibers for electric devices with motion sensitivity and flame retardance**

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Integration of conductive nanomaterials into flexible bio-based fibers with multi-functionality remains challenging due to interface failure, poor flexibility and inflammability. Although having broader applications in textiles, regenerated cellulose fiber (RCF) can’t meet the requirements of wearable electronics owing to their intrinsic insulation. Herein we showed that conductive RCF fabricated by coordinating of copper ions with cellulose and reducing into stable Cu nanoparticles coated on their surface. The Cu sheath offered excellent electrical conductivity and enhanced flame retardance. Conductive RCF
as wearable sensors for human-health detection and motion monitoring. The resultant fibers not only offer stable conductive nanocomposite on fiber surface, but also offering huge potential for wearable devices, smart sensors and flame-retardant circuits.

CELL 3915130

Surface diffusion barrier strategy toward water-resistant photonic materials for accurate detection of ethanol

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Photonic materials that enable visual detection of chemicals have shown great potential for wide applications in chemical, environmental, biotechnological, and food industries, but until now, using hydrophilic photonic materials for tracing water-soluble chemicals remains a major challenge due to the strong water interference. Here, we demonstrate a two-step co-assembly and subsequent surface coating strategy to develop an ethanol-sensitive and anti-water interference photonic crystal film. By using citric acid as a co-assembly phase, high ethanol sensing is realized because of the strong intermolecular affinity. By controlling the thickness of the outer polyvinyl butyral layer, selective ethanol penetration but a water barrier is enabled. Notably, the composite photonic films are free-standing, highly flexible, and controllably structurally colored. We further present using the composite film to quantitatively trace ethanol/water mixtures and potentially track drunk driving as a colorimetric sensor. The heuristic two-step modification strategy proposed in this work not only overcomes the limitation of water interference for hydrophilic colorimetric sensors but also provides references to develop more new photonic materials with water resistance that need to be applied in water/humid environments.

CELL 3916113

Hierarchically structured sustainable composites for wearable strain sensor applications

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It has been widely accepted that sustainable polymers such as cellulose derived from renewable resources are able to replace the short-turnover petroleum-based materials and reduce environmental impact in the future. How to fabricate advanced multifunctional composites based on these renewable sources through hierarchically structure design is attracting highly interests around the world. Here, we focus on the multi-scale
nanostructure design and environment-friendly processing of sustainable composites, and carry out a series of works about multifunctional materials and devices. Bio-sourced raw materials including cellulose, tannic acid, natural rubber were utilized to fabricate wearable strain sensors. In detail, by using cellulose nanocrystals as template an one-dimensional Ag nanohybrid was produce by a simple and green strategy and then com- posited with natural rubber for the strain sensing application; Three different nanostructure including randomly dispersed structure, segregated structure and layer-by-layer structure were fabricated, and a visualized simulation strategy for the analysis of structural evolution was also proposed, guided by the visualized analysis, nanocomposites with a desired balance between sensitivity and working range were achieved; By applying the mechanoluminescence foam-coating on conductive cotton fabric, a multifunctional composite material with piezoresistivity and mechanoluminescence properties was successfully fabricated for a wearable sensor. These works not only provide valuable examples for the design of advanced wearable strain sensors based on renewable materials, but also open up new opportunities in the design of advanced intelligent materials and reduce environmental impact in the future.

CELL 3915256

Facile preparation of ultrafine and fairly long carboxylated cellulose nanofibers

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Sustainable carboxylated cellulose nanofibers (C-CNFs) with access to variable surface chemical modifications and exquisite mechanical properties have great and promising applicability across various fields. However, the current fabrication processes either require harsh reaction conditions or severely impair the high aspect ratio of products, resulting in low yields, environmental issues and/or limited uses. Herein, we address these limitations by using a hydrated multi-carboxylic acid deep eutectic solvent (H-DES) comprised of only choline chloride, citric acid, and water to produce ultrafine and fairly long C-CNFs. The resultant C-CNFs have fine diameters of ~3.4 nm, high aspect ratios up to 2500, high carboxyl content of 1.5 mmol/g, and high mass yield of 90.12%. Superior stability of the C-CNFs suspensions even at high concentrations allows their easy storage, transportation, processing, and utilization. Notably, life cycle assessment (LCA) further demonstrates the economic feasibility and sustainability of the process, it proves that we can easily achieve large-scale production of C-CNFs for preparing large-area, high-performance structural materials. These unique advantages open up a new route to produce ultrafine C-CNFs on an industrial scale.
**CELL 3914912**

**Metal–organic framework derived copper catalysts for efficient hydrogenolysis of lignin into monomeric phenols**

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Reductive catalytic fractionation (RCF) of lignocellulosic biomass has emerged as a leading lignin valorization strategy. Herein, we present a copper-based catalyst (CuO/C) derived from a metal organic backbone (HKUST-1) with excellent catalytic performance for RCF of woody sawdust, which afforded high yields of propyl and propanol end-chain monomeric phenols (15.5 wt% in softwoods and 46.7 wt% in hardwoods) via C–O bond scission. A series of conifer β-O-4 models and their deuterated analogues revealed that the synergistic action of CuO/C and hydrogen could effectively cleave aryl ether linkages. It was deduced that lignin alcoholsysis led to partial α-OH etherification of the β-O-4’ units, which promoted C–O bond breakage of Cα-OMe and Cβ-O, thus giving propanol phenolic compounds through hydrogenation of coniferyl alcohol over CuO/C catalyst. When both α- and γ-OH of β-O-4’ motifs were meoxylated, the para-propyl phenolics were obtained though the scission of C–O linkages (Cα-OMe and Cβ-O), followed by Cγ-OMe cleavage of propenyl ethers and hydrogenation of propenyl phenols. We envision that this work may pave the way for the development of non-noble catalyst with high reactivity and selectively for lignin valorization.

**CELL 3916255**

**Hofmeister effect assisted high-performance organohydrogels with enhanced ionic conductivity, balanced mechanical properties and long-term environmental stability for flexible sensors**

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Recently, ionic conductive hydrogel based flexible sensors have attracted great interest from researchers. However, the simultaneous incorporation of conductivity, mechanical robustness and the ability to adapt to extreme environments remains a grand constraint.
Herein, a novel conductive dual-dynamic-bond cross-linked platform was proposed by designing skin-inspired ionic organohydrogels based on Hofmeister effect and oil/water system. Due to the efficient integration of different components and enhanced salting-out effect, the organohydrogel with interpenetrating network structure and multiple physical interactions simultaneously realized balanced conductivity, mechanical strength and versatile properties. Firstly, the organohydrogel successfully balanced the inherent contradiction between ionic conductivity and mechanical properties assisted by Hofmeister effect. Kosmotropes and chaotropes regulated the aggregation state of polymer chains, and further affected the water content and pore structures, finally realizing the continuously in-situ modulation of mechanical properties and ionic conductivity over a large window: conductivity from 0.08 to 4.8 S m⁻¹, strength from 0.01 to 17.30 MPa, toughness from 5.4 to 9236.9 kJ m⁻³ and modulus from 5.1 to 2258.9 kPa. Furthermore, glycerol/water system exhibited low temperature tolerance and long-term stability, which provided conditions for the normal operation in harsh environment. The hydroxyl group on glycerol acted as the hydrogen bond donor and interacted with water molecules to form a dense hydrogen bond structure, which interfered with the freezing process of water molecules and reduced the vapor pressure of water. Finally, the organohydrogel with these characteristics realized real-time monitoring of human subtle movements and large-scale activities, which exhibited broad application prospect in the fields of wearable flexible sensors and artificial electronic skin. In short, this study provides a simple strategy for the controllable adjustment of conductivity and mechanical properties of ionic conducting hydrogels and a new idea for the manufacture of a new type of intelligent sensor based on multifunctional hydrogels.

CELL 3919916

Controllable preparation and material properties of novel thiolated cellulose esters

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Cellulose esters are important cellulose derivatives with good processing properties and material properties. The design and sustainable synthesis of cellulose esters are prime research topics. The transesterification reaction between cellulose and methyl 3-mercaptopropionate is considered to be a simple and green strategy for the synthesis of thiolated cellulose esters. Thiolated cellulose esters are simply prepared by an atomic economy reaction between cellulose and methyl 3-mercaptopropionate dissolved in a newly developed 1.8 diazabicyclo [5.4.0] undecan-7-ene/dimethyl sulfoxide/carbon dioxide solvent system without the addition of any external reagents or catalysts. It was further modified to add mercapta to its surface. Multifunctional compounds were synthesized through post modification reactions and the use of thiol-ene and thiol-Michael addition reactions. At the same time, the reaction parameters (i.e. concentration, temperature, methyl 3-mercaptopropionate equivalent, and reaction time) were optimized. The structure and thermal properties of thiolated cellulose esters were characterized by nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, differential scanning calorimetry, and thermogravimetric analysis, to develop an in-depth understanding of the correlations among the chemical structures, thermal properties, and mechanical properties.
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**Flame-retardant fibre-particle-polymer semiconductive networks for physically transient supercapacitors and chemiresistors**

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With fast development of green economy and carbon neutral society, biodegradable and sustainable materials are urgent needed for multifunctional transient electronics. Here, a flexible, biodegradable and flame-retardant fibre-particle-polymer network is developed for physically transient supercapacitors and chemiresistors. By regulating 1D-0D-2D ternary interface, micro/nanoarchitected polyaniline/ink/alginate semiconductive network enables effective electrolyte infiltration and abundant surface adsorption and diffusion. Moreover, the 0D ink particles promote interface bonding between 1D alginate fibres and 2D polyaniline, giving rise to better wear resistance, compression-after-impact strength and electrical conductivity. As expected, the transient supercapacitor delivers high areal capacitance of 134.1 mF cm\(^{-2}\), and the transient gas sensor exhibits desirable response (33%) and long-term stability (56 days) toward 40 ppm NH\(_3\) at room temperature, which is superior to most of previous reports. This work pushes forward a significant step towards fibre-particle-polymer interfacial design of physically transient electronics and shows great potential in flexible platform based on comfortable biofibers.

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**Low-cost ionic liquids based synthesis of biomass derived carbon dots**

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As one kind of promising zero-dimensional advanced biomass nanomaterials, biomass derived carbon dots (CDs) have attracted extensive attention recently in green chemistry and engineering on account of their excellent properties, such as water solubility, comparable optical properties, low toxicity, and surface passivation and functionalization. However, the separation and extraction of raw biomass material often requires the use of mineral acids and bases, leading to significant material loss, equipment corrosion, and environmental pollution. In recent years, as a new type of functional medium, ionic liquids (ILs) have been increasing reported in the preparation, modification, and application of advanced biomass materials because of their controllable structure, adjustable function, and effective solubility of biomass. Based on the above background, we prepared nitrogen and sulfur doped CDs from cellulose by a one-pot ionothermal method in the presence of low-cost sulfonic acid-type eutectic ILs (DES). We used the prepared CDs to construct “turn off” fluorescent probes for Cu\(^{2+}\) (0–1.72 μM) and “turn on” fluorescent probes for glutathione (20–400 μM). The CDs have good tolerance to pH, ionic
strength, and storage time, so they have great potential for detection applications in wa-
ter samples in different environments. In addition, due to the advantages of the ionother-
mal synthesis with lower requirements on reaction devices and reaction conditions, a
large number of types of ILs reaction media and media recyclability, this method pro-
vides a more efficient and low-cost way for the preparation of CDs. Then we chose glu-
cose to further explore the effect of DESs on the fluorescence characteristics of CDs.
The fluorescence emission of CDs can be shifted from blue light to green light by chang-
ing the structure of sulfonic acid-type DES, reaction temperature and time. The types
and proportions of hydrogen bond acceptor and hydrogen bond donor used in DES have
an impact on the UV-Vis absorption peaks and fluorescence emission peaks of CDs.
Based on the characterization results, it was found that the reason for the red shift of the
fluorescence emission spectrum of CDs is mainly the result of the combined effects of
size, graphitization degree, and surface state.

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**Skin-mimicking strategy to fabricate strong and highly conductive anti-freezing
cellulose-based hydrogels as strain sensors**

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Conductive hydrogels have attracted increasing attention for applications in wearable
and flexible strain sensors. However, owing to their relatively weak strength, poor elas-
ticity, and lack of anti-freezing ability, their applications have been limited. Herein, we
present a skin-mimicking strategy to fabricate cellulose-enhanced, strong, elastic, highly
conductive, and anti-freezing hydrogels. Self-assembly of cellulose to fabricate a cellu-
lose skeleton is essential for realizing a skin-mimicking design. Furthermore, two meth-
ods, in situ polymerization and solvent replacement, were compared and investigated to
incorporate conductive and anti-freezing components into hydrogels. Consequently,
when the same ratio of glycerol and lithium chloride was used, the anti-freezing hydro-
gels prepared by in situ polymerization showed relatively higher strength (1.0 MPa),
while the solvent-replaced hydrogels exhibited higher elastic recovery properties (94.6
%) and conductivity (4.5 S/m). In addition, their potential as strain sensors for monitoring
human behavior was analyzed. Both hydrogels produced reliable signals and exhibited
high sensitivity. This study provides a new horizon for the fabrication of strain sensors
that can be applied in various environments.