ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE
January 1, 2019 – December 31, 2019
Project RU-9

PROJECT TITLE: Strategies leading to novel nano-materials and performance industrial products

PROJECT LEADER: You-Lo Hsieh
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LEVEL OF 2019 FUNDING: $117,358

OBJECTIVES AND EXPERIMENTS CONDUCTED TO ACCOMPLISH OBJECTIVES:

This project is to develop efficient processes to isolate rice straw components and convert them into high value novel nanomaterials and advanced functional products. Effort for 2019 was focused on further discover and expand the high performance product development and technology transfer of existing rice straw nanomaterial technologies (UC Cases No.):

No. 2016-909 Ultra Light Amphiphilic and Resilient Nanocellulose Aerogels and Foams (Provisional 03.29.2018)(U.S. Patent Application filed March 22, 2019**)**
https://techtransfer.universityofcalifornia.edu/NCD/27150.html

No. 2017-364 Butadiene Sulfone as a Green Multi-Functional Telomerization Agent for Tunable Hydrophobic Nanocellulose (Provisional 03.27.2017)
https://techtransfer.universityofcalifornia.edu/NCD/27619.html

No. 2018-809-0 Conducting Nanocellulose Aerogel Strain Sensor
(Provisional Patent 05.14.2018)
https://techtransfer.universityofcalifornia.edu/NCD/29536.html

No. 2019-302 Aqueous Exfoliated Graphene by Amphiphilic Cellulose Naofibrils for Foldable and Moisture-Responsive Nanopaer (Provisional 10.26.2019) (International Patent Application filed October 28, 2019)
https://techtransfer.universityofcalifornia.edu/NCD/30089.html

No. 2020-030-1 Coaxial Cellulose-based Aerogel Fibers
(Record of Invention ROI 08.15.2019; provisional application authorized 09.05.19)

Objectives 1**: **Nanocellulose aerogel structural and functional product development

1a. Aerogel core and porous sheath fibers via wet spinning for thermal insulation
(2020-030-1 Coaxial Cellulose-based Aerogel Fibers, New provisional patent application**)**

Rice straw based nanocellulose aerogels we have invented have many unique attributes that differentiate from commercially available hydrophilic, but friable, silica aerogels as well as strong, but hydrophobic carbon nanomaterial (graphene, carbon nanotube) based aerogels. Further shaping these nanocellulose aerogels into desired forms and dimensions has targeted the most challenging engineered forms, i.e., fibers, so they can be fabricated into flexible mats, woven, knitted and nonwoven wearable materials for thermal protective applications. Highly porous and strong cellulose-rich coaxial fibers have been successfully engineered to consist of the multiscale porous sheath and nanocellulose aerogel core as novel thermal insulation materials.

Strong, continuous, and highly porous coaxial fibers with cellulose nanofibril aerogel core and cellulose-rich sheath were fabricated by wet-spinning hollow fibers and infusion of aerogel precursor. The sheath contained multiscale pores, including microvoids (15 ± 13 µm) and sub-micron pores (133 ± 49 nm) in bulk, as well as nanopores (ca. 25 nm) on both inner and outer surfaces, to function as a template and protective surface layer for the CNF aerogel core. The porous coaxial fibers had many desirable qualities, including low density (0.2 g cm3), high porosity (85%), high specific tensile strength (23.5 ± 2.5 MPa g cm^{-3}), wide working temperature range (-20 to 150 ◦C), continuous and large-scale producibility, as well as biodegradability. The unique combination of multiscale porous sheath and ultra-low density aerogel core synergistically restrain air circulation to limit convective heat transfer, while the poor conducting cellulose permitting little conductive heat transfer and the highly crystalline aerogel cellular walls prohibit infrared radiation, effectively suppresses heat transfer via all three mechanisms under extreme temperatures.

Figure 1. CNF aerogel core-porous cellulose sheath fibers: (top) morphologies and microstructures of hollow and coaxial fibers by SEM; (bottom) thermal insulation mechanisms.

1b. Diversification of aerogels via ionization and/or protonation of nanocelluloses
(expand Provisional and U.S. Patent Application filed March 22, 2019)

All variety of aerogels developed from this project have been from CNFs synthesized from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation, including amphiphilic aerogels, crosslinked hydrophobic aerogels, and thermally stable and strong CNF-silica aerogels. The ionic nature of these CNFs and aerogels were further explored by altering the charged nature or protonation of CNFs to different levels to study their effect on aerogel properties. As these aerogels of highly hydrophilic and charged to varying degrees, liquid transport and easily tunable surface chemistries would allow future development related to electrolyte and ion exchange membranes with potential applications.

We have created nanocellulose aerogels CNFs synthesized from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation via ice-templating, i.e., slow freezing to nucleate and grow ice crystals. The amphiphilic nature of these aerogels have been expanded to be tunable hydrophobic by crosslinking and more thermally stable and strong by in-situ synthesis of CNF-silica aerogels. Protonation of aqueous CNF has shown to improve shape retention of aerogels (Figure 2), however, seems to lower dry and wet compression strength. Further work continues to clarify such effect on structural changes.

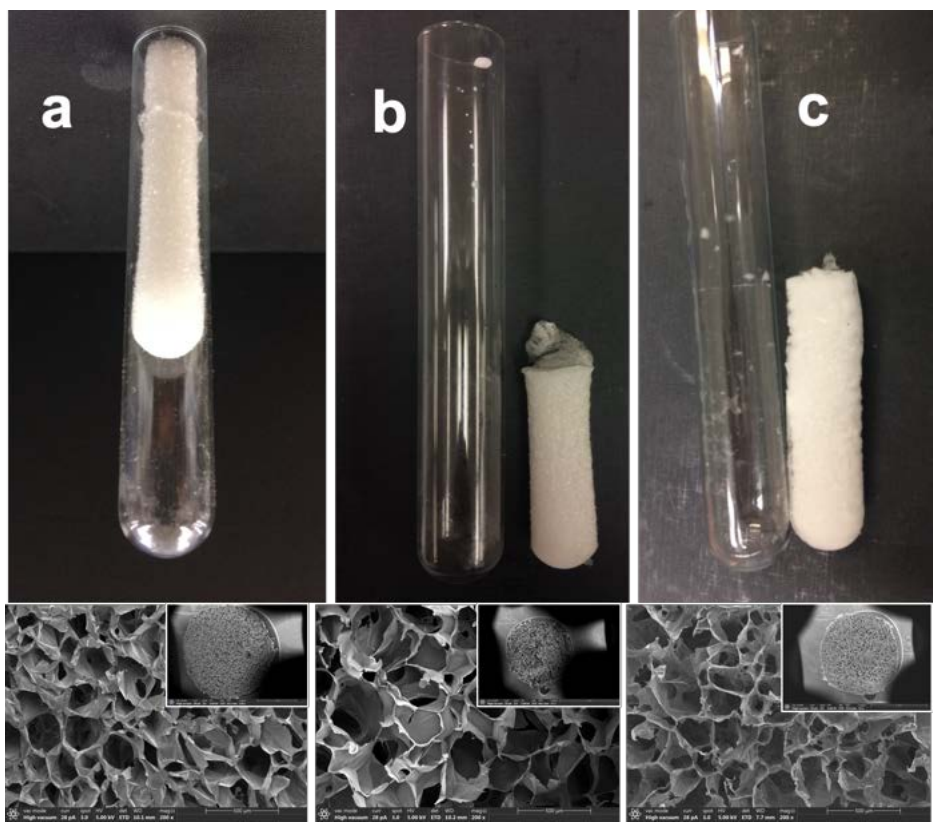
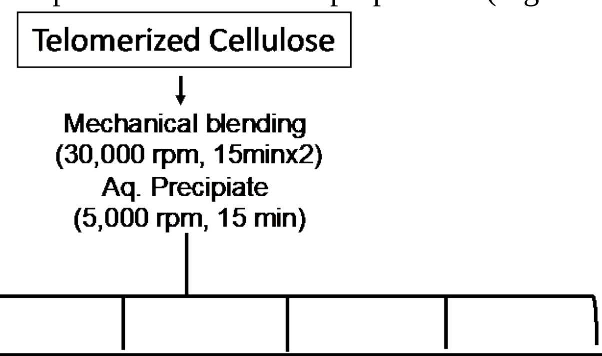


Figure 2. Aerogel shape retention as affected by protonation: (a) 11% (b) 46% (c) 100% COOH.

Objectives 2: Tunable amphiphilic/hydrophobic nanocellulose structural and functional product development *(expand provisional patent* 2017-364*)*

A novel and green approach has been successfully developed and validated to produce a diverse range of tunable hydrophobic to amphiphilic nanocelluloses. This process uses a multi-functional, recyclable butadiene sulfone (BDS) as solvent, reagent, and acid precursor. This new multi-functional solvent and reagent reduce the use of chemicals by serving as the reactant to telomerize with cellulose as well as the solvent phase to produce ether functional groups on C2, C3 or C6 hydroxyls of anhydroglucose unit at 100% atomic efficiency, thus an elegant way to synthesize stable ethers with minimal environmental impact.

The ODE- nanocelluloses (NCs) are similar in crystallinity and thermal stability as cellulose, significantly advantageous over those by other chemical processes, notably acid hydrolysis and oxidation. ODE-NCs have unique surface chemistries and tunable amphiphicity/hydrophobicity different from all other nanocelluloses by current existing processes. The tunable, amphiphicity/hydrophobicity of ODE-NCs makes these nanocellulose more versatile and compatible with organic liquids and other polymers/plastics. In 2019, the current high speed blending to break apart ODE-cellulose in aqueous media was replaced by sonicating ODE-cellulose in organic liquids by sonication to evaluate the potential to simultaneous difibrilate and mixing with other polymers and oils. Depending on the media, both ODE-cellulose nanofibrils (CNFs) and nanoparticles (NPs) were produced in different proportions (Figure 3).



	m-Cresol	DMF	DMSO	THF	CHCl3	Toluene
*wt% SN (n=5):	33.3 ± 4.7	19.6 ± 6.5	41.6 ± 10.0	27.3 ± 3.4	30.3 ± 8.9	28.1 ± 13.0
**AFM height (nm), n=50:	d:12.0 ± 8.9	d:	2.4 ± 3.6	6.3 ± 2.4	4.4 ± 2.2	N/A
NP/CNF (% area):	99/1	90/10	50/50	40/60	30-50/70-50	N/A

*Wt% of the organic supernatant is based on the aqueous precipitate as 100 %.
** AFM height was measured on graphite.

Figure 3. Organic dispersible ODE-NCs

Objectives 3**: **Nanocellulose exfoliated graphene functional product development
(expand **2019-302** Provisional 10.26.19 & International Patent Application filed October 28, 2019)

CNFs synthesized by TEMPO-mediated oxidation have shown to be surface-active to function as emulsifing and exfoliating agents as well as self-assemble into amphiphilic fibers, films and aerogels. CNF film has shown to have a uniquely large coefficient of hygroscopic expansion (CHE) of 3.8 ppm K^{-1}. Graphene on the other hand has high light harvesting quality. Here, we combine the high light harvesting "dark" graphene with high CNE CNF to create light-responsive actuator.

The new effort further optimizes CNFs as agents for aqueous exfoliation to produce graphene and exploit the resulted CNF-bound graphene precursors for new performance products. Herein, we design bilayer actuators that operate based on the large hygroscopic contraction of the CNFs and simultaneously small thermal expansion of the graphene upon increasing the temperature. Different from the traditional bilayer designs that consist of an active layer bonded to a passive layer, our bilayer actuators are composed of two active layer materials, i.e., CNF and graphene, respectively. The foldability and anisotropic behavior of the CNFs allow a series of programmable self-organization of graphene. Such CNF-activated graphene deposition on substrate functions with large bending and fast responding rate.

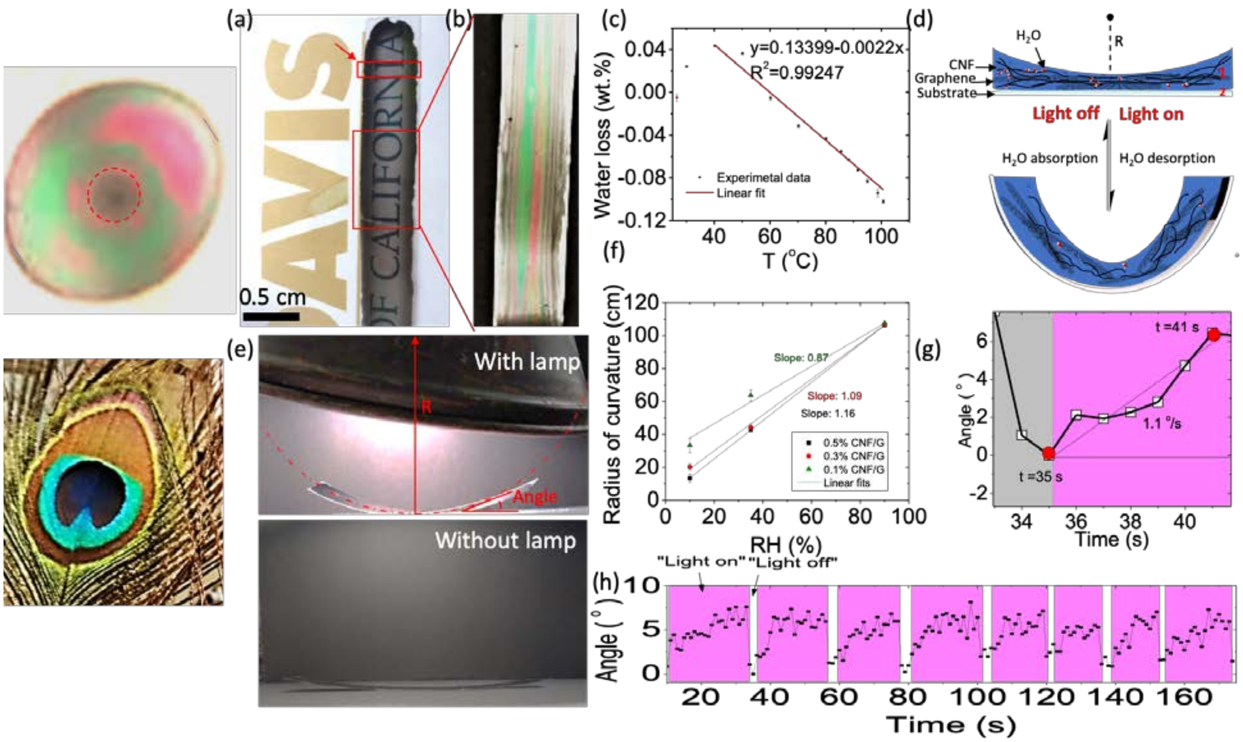


Figure 3. Photothermal graphene/CNF thin film actuator: **(a)** Photos of a graphene/CNF (0.1%, 2 mL, 1×10 cm^2) on ITO/PET substrate); **(b)** Zoomed area showing iridescent colors; **(c)** Water loss with respect to temperature; (**d**) Sketch of the bilayer graphene/CNF thin film photothermal actuator; **(e)** Photos of a representative actuator bending with light on and recovering with light off; **(f)** Radius of curvature of actuators with different graphene/CNF thicknesses (0.5%, 0.3%, 0.1% concentrations, 1 mL); (**g**) Bending angles in one cycle; (**h**) multi-cycles of angular changes of the same sample via light irradiation.

Major scientific advancement on rice straw nanomaterial and advanced product development

Rice straw nanocellulose aerogels represent the most developed advanced materials from rice straw, reaching technical readiness level (TRL) 4. These nanocellulose aerogels are amphiphilic, i.e., capable of absorbing both polar (hydrophilic, aqueous) and none-polar (hydrophobic, hydrocarbon) liquids, and are the only currently known amphiphilic aerogels from any source including nanocellulose. This amphiphilic attribute is so unique that it distinguishes our rice straw nanocellulose aerogels from both the hydrophobic carbon (graphene or carbon nanotube) and the hydrophilic silica aerogels or those based on dissolved cellulose. To exploit potential products and applications from our provisional patent, timely effort is critical to target more specific applications of these strong, wet resilient, in both aqueous and organic media, and tunable amphiphilic to hydrophobic aerogels. Further development of rice straw nanocellulose aerogels in 2019 includes the following potential directions:

- Highly porous and strong cellulose-rich coaxial fibers have been successfully engineered to consist of the multiscale porous sheath and nanocellulose aerogel core as novel thermal insulation materials.
- Protonation of TEMPO-CNF has shown to improve shape retention of aerogels.
- Hydrophobic ODE-cellulose can be defibrillated in organic liquids by sonication into a combination of ODE-nanofibrils and ODE-nanoparticles.
- Photonic thin CNF-graphene films have been fabricated to behave as light-responsive actuator.
- In 2019, one paper was published in a refereed journal, two refereed journal papers are in review and two manuscripts are in preparation.
- The PI has also made a total of 13 oral presentations, either of which were invited, including 3 keynote and 5 international, including China, Japan, Finland, Portugal and Taiwan.

Technology development and outreach on rice straw nanomaterial applications:

- The PI was invited to present rice straw nanocellulose technologies at the Cellulose Nanomaterials Researchers Forum at the University of Maine in August. The University of Maine Process Development Center houses the only nanocellulose processing facility in the US servicing both wood pulp, paper and a broad range of industry interested in nanocelluloses.
- Three global companies and two startups have signed Confidential Disclosure Agreements (CDA) and begun discussions on developing rice straw nanocellulose and nanosilica based products.
  - Rice straw nanocellulose aerogel has been tested for potential super-absorbent applications for the second year.
  - Four other inquires of potential applications have led to further discussions of technology development and transfer including one on rice straw nanosilica vapor absorbents, three on nanocellulose aerogels for health, automobile and insulation applications.
- Two new provisional patents filed in 2019: conducting nanocellulose aerogel strain sensor pm in May 2019 and coaxial nanocellulose aerogel core fibers in September 2019.
- Two new patents filed in 2019: US patent application on aerogels in March 2019, one international patent on nanocellulose exfoliated graphene in October 2019.
- Five provisional/US/International patents related to this RU-9 project are UC Case No.:

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CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

Hsieh's group has successfully optimized processes and exploited product strategies to valorize rice straw by creating an array of novel nano-materials and unique high performance products. The most diverse array of nanocelluloses, including rod-like cellulose nanocrystals and super thin and long cellulose nanofibrils, with tunable surface chemistries and charges have been facilely fabricated from rice straw cellulose, representing the most diverse nanocelluloses from a single source among agricultural biomass. These comprehensive choices of nanocelluloses have been demonstrated as oil dispersants, antimicrobial agents, microbial coagulants, synthesis templates for nanoparticles, and aqueous exfoliating agent for graphene as well as nano-building blocks to fabricate a range of fibers, films, coatings, hydrogels and aerogels. Proof of concept has been demonstrated in applications of these advanced materials for oil-water separation, water purification, organic solvent/hydrocarbon removal or oil clean up, catalyst and amphiphilic films and coating technologies, conducting aerogels and moisture responsive nanopaper, photothermal actuator, to name a few. In 2019, one U.S. patent was filed on March 22, one international patent application filed October 28, 2019 and one new Record of Invention for provisional patent (UC Case No. 2020-030-1 Coaxial Cellulose-based Aerogel Fibers) was filed on August 14. Together, five total provisional patents, two each in 2017 and 2018 as well as one in 2019, have been filed.

PUBLICATIONS: one published, two in review, and two in preparation

Xu, X., Y.-L. Hsieh, Aqueous Exfoliated Graphene by Amphiphilic Nanocellulose and its Application in Moisture-responsive Foldable Actuators, *Nanoscale*, 2019, **11**, 11719 – 11729.

Zhou, J., Y.-L. Hsieh, Nanocellulose Aerogel-based Porous Coaxial Fibers for Thermal Insulation, Nano Energy (In Press).

Xu, X., Y.-L. Hsieh, Cellulose Nanofibril Photonic Thin Films and Photothermal Actuator, In review.

PRESENTATIONS: 13 (8 invited including 3 keynote and 5 international)

Hsieh, Y.-L., Nanocellulose innovations: hierarchical structures, tunable amphiphilicity and chemical functionalities, **Invited Keynote**, Nanocellulose Research Starting from Domestic, Foreign Countries and Regions Symposium, 8th PHOENICS International Symposium and 4th IROAST Symposium "International Symposium on Chiral Nano-composite, Kumamoto University in Kumamoto, Japan, January 24-26, 2019.

Hsieh, Y.-L., **Invited,** Sustainable nanomaterial innovations, Proctor and Gamble, Cincinnati, Ohio, March 15, 2018.

Hsieh, Y.-L., 1D to 3D hierarchical structural materials from biomass, Division of Cellulose and Renewable Materials, ACS National Meeting, Orlando, FL, March 31, 2019.

Hsieh, Y.-L., Tunable and green processing innovations, Nanocellulose Workshop, Washington, DC, May 7-8, 2019.

Hsieh, Y.-L., **Invited,** Material innovations: from tunable chemical functionalities to hierarchical structures, HYBER-FinnCERES Symposium, Helsinki, Finland, May 15-17, 2019.

Hsieh, Y.-L., Nanocellulose aerogels for CO_2 capturing and conducting strain sensors, 2019 International Conference on Nanotechnology for Renewable Materials, TAPPI, Chiba, Japan, June 3-7, 2019.

Hsieh, Y.-L., **Invited**, Cellulose innovations: from nanoscale to novel functions, International Conference on Natural Fibers (ICNF), Porto, Portugal, July 1-3, 2019.

Hsieh, Y.-L., **Invited Keynote,** Advanced fibrous materials from under-utilized biomass, 2019 International Conference on Eco-Textiles (ICET2019), Jiangnan University, Wuxi, China, August 4-6, 2019.

Hsieh, Y.-L., **Invited Keynote**, Biomass to functional nanofibers: chemically functionality and hierarchical structures, International Symposium of Renewable and Sustainable Materials, Materials 2019, Taipei, Taiwan, August 8-10, 2019.

Hsieh, Y.-L., Western Sun Grant Wrap Up meeting, Western Sun Grant Center, Newport, Oregon, August 21-22, 2019.

Hsieh, Y.-L., **Invited**, Cellulose Nanomaterials Researchers Forum, University of Maine, August 28-29, 2019.

Hsieh, Y.-L., **Invited,** Nanocellulose Innovations from Under-utilized Agricultural Biomass, 4^{th}International Symposium on Materials from Renewables (ISMR 2019), University of Georgia, October 9-10, 2019.

Hsieh, Y.-L., Assembling 1D Nanofibers to 3D Hierarchical Functional Materials, The Fiber Society, University of Texas, Austin, October 28-30, 2019.