ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE
January 1, 2017 – December 31, 2017
Project RU-9

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

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LEVEL OF 2017 FUNDING: $102,997

OBJECTIVES AND EXPERIMENTS CONDUCTED TO ACCOMPLISH OBJECTIVES:

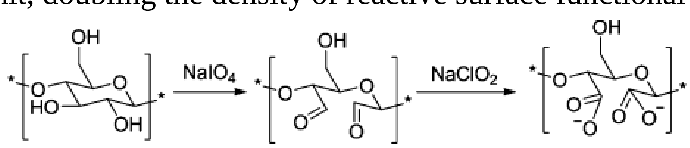
The overall objective of this project is to develop efficient processes to isolate rice straw components and convert them into high value novel nanomaterials and advanced functional products. The goals for 2017 were to continue the development of scalable processes and to expand functional applications of nanocellulose and porous carbon products.

The specific objectives in 2017 were to:
1. *Diversify CNF structures via sodium periodate oxidation and mechanical shear*
2. Simultaneous isolation and utilization of cellulose and silica in rice straw
3. Optimize aerogel properties and processes into scalable industrial/consumer products
4. Develop new green process to generate hydrophobic cellulose nanofibrils

The experiments conducted and results obtained to achieve these objectives are summarized as follows:

Objective 1. *Diversify CNF structures via sodium periodate ($NaIO_4$) oxidation and mechanical shear*

Rice straw cellulose were chemically modified by sodium periodate ($NaIO_4$) and sodium chlorite ($NaClO_2$) oxididtion and mechanically blended into nanocelluloses. As shown below, sodium periodate, $NaIO_4$, opens saccharidic ring at vicinal diol C2-C3 to generate di-aldehydes. Further oxidation with sodium chlorite ($NaClO_2$) converts the di-aldehyes into two C2 and C3 carboxyls per anhydroglucose unit, doubling the density of reactive surface functional groups.



Previously, primary oxidation (55 °C, 4 h) of rice straw cellulose with $NaIO_4$ at 0.25:1, 0.5:1 and 0.75:1 $NaIO_4$:anhydroglucose unit (AGU) followed by reaction with sodium chlorite at 1:1 $NaClO_2$:AGU (0.5 M acetic acid, room temperature, 48 h) produced nanofibrls (CNFs) $\leq$ 0.5 $NaIO_4$:AGU and nanocrystals (CNCs) at 0.75 $NaIO_4$:AGU. The yields are dependent on the extent of both oxidation and blending. In 2017, the yields and qualities of nanocelluloses were further optimized by varying both the primary $NaIO_4$ and secondary $NaClO_2$ oxidation reaction conditions.

For CNCs generated at 0.75 $NaIO_4$:AGU ratio, the yields were improved from 54.7% to 70.8 % by shortening the secondary oxidation reaction from 48 h to 24 h while surface charges could be raised to 1.4 mmol/g at longer reaction time (48 h) at 1:1 $NaClO_2$:AGU and a even higher 1.96 mml/g at higher 2:1 $NaClO_2$:AGU and 48 h, both at the expenses of lower yields (Table 1). Currently, these two step oxidation procedures are further optimized to 95.9% yield. Characterization of CNFs are on going.

Table 1. Yields and charges of nanocelluloses from $NaIO_4$ & $NaClO_2$ oxidation at varied concentration and time and blending of rice straw cellulose.

$NaIO_4$:AGU=0.5:1, 55°C, 4h

$NaClO_2$:AGU 0.5 M acetic acid RT	Blending	15 min-1st	15 min-2nd	30 min	15 min-3rd	15 min-4th	60 min	Precipitate
0.5:1 4 h	Yield (%)	15.7	6.14	21.8	7.70	4.10	33.6	--
	COOH (mmol/g)	1.12	0.54		0.32	0.44		--
0.5:1 8h	Yield (%)	18.9	5.6	24.5	8.80	7.0	40.3	--
	COOH (mmol/g)	1.59	0.89		0.82	0.56		--
1:1 4 h	Yield (%)	23.7	4.0	27.7	11.0	10.1	48.8	--
	COOH (mmol/g)	1.98	0.91		0.73	0.47		--

$NaIO_4$:AGU=0.75:1, 55°C, 8h

$NaClO_2$:AGU	Blending	15 min
1:1, RT, 12h	Yield (%)	70.90
	COOH (mmol/g)	1.14
1:1, RT, 24h	Yield (%)	64.70
	COOH (mmol/g)	1.35
1:1, RT, 48h	Yield (%)	54.70
	COOH (mmol/g)	1.4
2:1, RT, 48h	Yield (%)	47.0
	COOH (mmol/g)	1.96

This two-step $NaIO_4$ and $NaClO_2$ oxidation approach has been established and proven to be highly effective in generating both CNCs and CNFs by simply tuning the primary $NaIO_4$ reaction conditions and in optimizing yields and surface charges by controlling the secondary $NaClO_2$ oxidation conditions. The CNCs produced are not only in higher yields, but also carry carboxyl surface functional groups as opposed to the sulfonate groups from the typical sulfuric acid hydrolysis. A range of CNCs and CNFs with potentially more highly decorated carboxyl surface groups than the 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO) method may be produced. Further reaction optimization to establish charge and yield relationship as well as characterization of CNFs will continue in 2018.

***Objective 2**. Simultaneous isolation and utilization of cellulose and silica in rice straw*

This objective is to more fully utilize the two major rice straw components, i.e., ca. 38 % cellulose and ca. 15% silica, valorize over 53% of rice straw and to develop new nanocellulose based materials. This approach also takes the advantage of the complementary qualities of cellulose and silica, i.e., the most resilient but less thermally stable nanocellulose and the most heat resistant but brittle silica, to create more superior nanocellulose-silica aerogel composites.

CNF/silica hydrogels were first fabricated *via* a sol-gel process by aging aqueous CNF and sodium silicate precursors in varied ratios. Gelation was spontaneous as indicated by the higher G' than G'' upon mixing and continue during aging (Figure 3). G' decreased with lowering CNF contents and over time, suggesting that CNFs provide the primary skeletal gel structure while the condensed colloidal silica serves to bridge and interconnect CNFs within the gel networks. These CNF/silica hydrogels may be strengthened by adding HCl, solvent exchanged to tert-butanol and then freeze-dried. The pore structure and mechanical properties of CNF/Silica aerogels are being characterized and the ability of these rice straw based CNF:silica aerogels to absorb carbon dioxide will be studied for potential CO_2 sequestering applications and expected to complete in 2018.

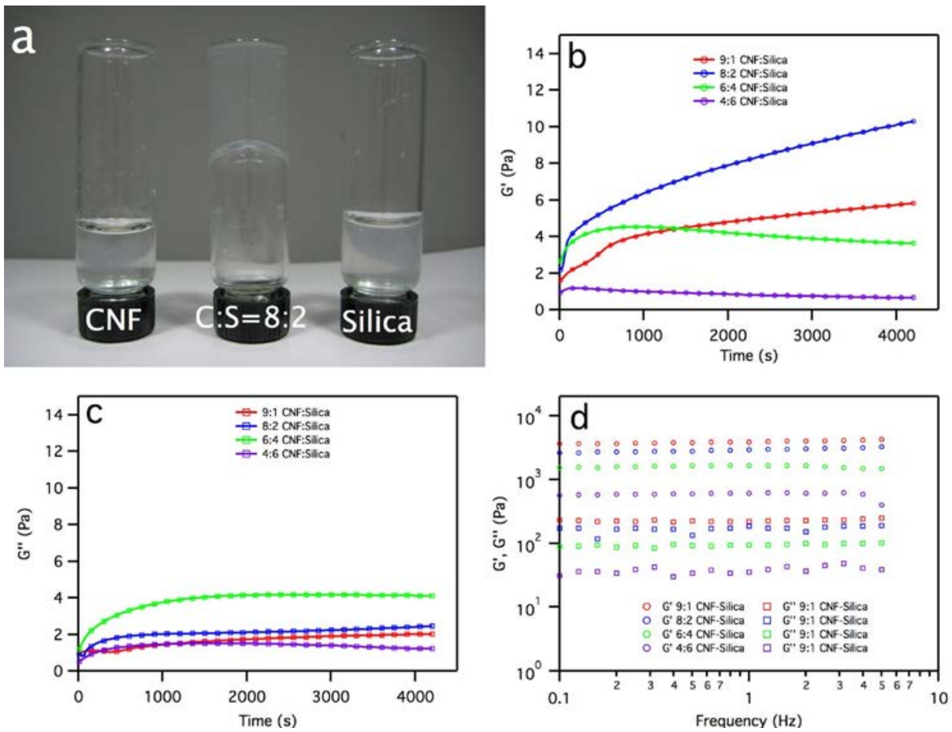


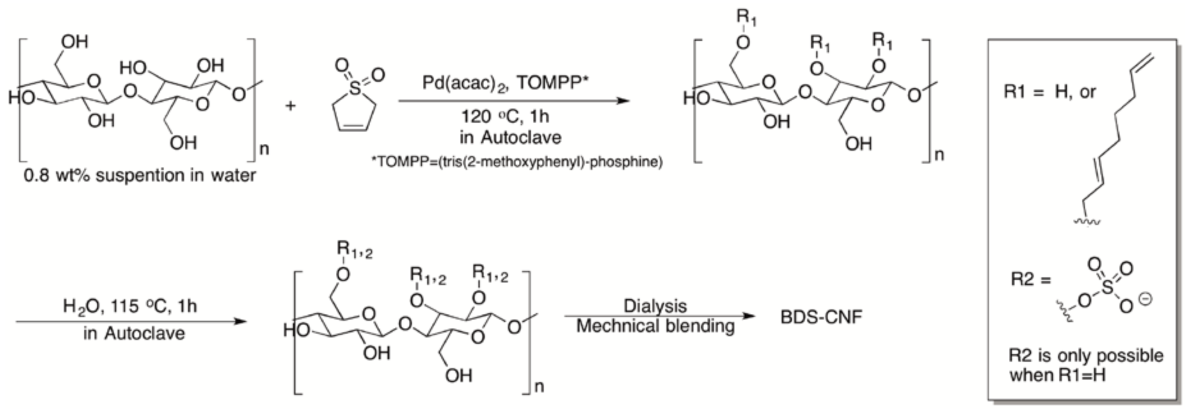
Figure 3. (a) Photo of 0.6 wt% of CNF, silica and 8:2 CNF:silica aged for 48 h; viscoelastic properties of CNF/silica hydrogel. (b) G' and (c) G'' of hydrogels during time sweep; (d) G' and G'' of hydrogels aged for 48 h aging and cured in 0.2 N HCl during frequency sweep.

Objective 3*. 3. Optimize aerogel properties and processes into scalable industrial/consumer products*

CNF based aerogels are among the most developed among all rice straw nanocellulose products and reach technology readiness level (TRL) 4. We have further refined the gelation and assembling processes for converting CNF into aerogels and also expanded the applications rice straw CNF aerogels for removal and recovery of cationic malachite green dye. Further crosslinking with diisocyanate has also synergistically improved the hydrophobicity, strength, thermal stability of CNF aerogels for cyclic removal of non-polar hydrocarbons from aqueous environment. Two papers have been published on these findings. Based on our published work and provisional patent on nanocellulose aerogels, potential interested product sponsors have been and will continue to be aggressively sought.

***Objective** 4. Develop new green process to generate hydrophobic cellulose nanofibrils*

We have tested and validated a new process to produce more hydrophobic nanocelluloses. This process uses a recyclable butadiene sulfone (BDS) as multi-functional reagent, solvent and acid source. At elevated temperatures above 95 °C and under pressure, BDS decomposes into 1,3-butadiene to telomerize cellulose in BDS as the solvent to produce 2,7-octadienyl ether functional groups on the hydroxyls of amorphous and crystalline surfaces of cellulose. Upon cooling, water is added to react with gaseous SO_2 byproduct to generate H_2SO_4 that facilitates the defibrillation of cellulose by disruption of hydrogen bonding, acid hydrolysis of 1,4-glycosidic bonds, and potential addition of charged sulfate esters on the remaining unreacted OH groups. The gaseous 1,3-butadiene and SO_2 re-form to solid BDS that can be recycled back and re-initiate telomerization.



Scheme 1: The reaction route for telomerization and acid hydrolysis to generate hydrophobic cellulose nanofibrils (BDS-CNF).

The cellulose nanofibrils (CNFs) generated are narrower than those produced by TEMPO-mediated oxidation we previously reported (Figure 4) but are far more thermally stable, a significant advantage. Work continues in optimizing both telomerization and hydrolysis reactions, the yield as well as detailed characterization of CNFs in 2018.

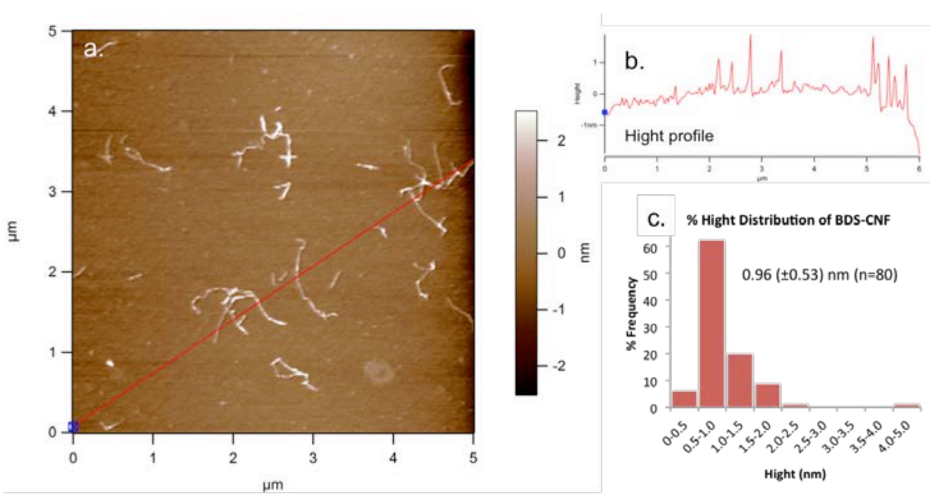


Figure 4: AFM image of BDS-CNF generated from the optimized reaction. (a) 0.0003 vol% BDS-CNF in aqueous solution. (b) Height profile. (c) % Width distribution of BDS-CNF with the average of 0.96 (±0.53) nm.

Major scientific advancement on rice straw nanomaterial and advanced product development

- A new surface oxidation approach using sodium periodate and sodium chlorite coupled with mechanical blending has been established to generate a range of nanocelluloses, i.e., cellulose nanocrystals and nanofibrils with surface C2 and C3 carboxyls, expanding from those with surface C6 carboxls by the TEMPO mediated oxidation method.
- Rice straw nanocellulose-silica aerogels have been prepared in varied compositions with the goals to valorize both cellulose and silica in rice straw and to take advantage of the complementary resiliency of cellulose and thermal stability of silica while advancing rice straw nanotechnologies.
- A green processing approach has been established to produce nanocelluloses with tunable surface amphiphilicies in rod-like cellulose nanocrystals (CNCs) and ultra-thin cellulose nanofibrils (CNFs). This break through innovation is the only one-pot process known to date for producing hydrophobic nanocelluloses.

Technology development and outreach on rice straw nanomaterial applications

- The PI was invited to make oral presentations on rice straw nanocelluloses internationally, including China, Japan, Portugal, Spain.
- Rice straw nanocellulose aerogel research was recognized by invitation to present at the American Chemical Society CELL Division and International Conference on Nanotechnology for Renewable Materials meetings.
- One provisional patent on green processing for nanocelluloses, were filed in March 2017 with another existing one on nanocellulose aerogels.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

This project has successfully optimized processes and exploited product strategies to valorize rice straw by creating an array of novel nano-materials and unique 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. These comprehensive choices of nanocelluloses have been demonstrated as dispersants, antimicrobial agents, microbial coagulants and synthesis templates for nanoparticles, as well as used as nano-building blocks to fabricate nanofibers, films, coatings, hydrogels and aerogels. From these advanced materials, proof of concept has been demonstrated for oil-water separation, water purification, organic solvent clean up, catalyst and amphiphic films and coating technologies, to name a few. In 2017, two provision patents were filed in addition to a total of 9 presentations of which 4 were invited, 3 refereed journal papers published and one additional in press.

PUBLICATIONS: 3 published (including 2 submitted in 2016), 1 in press, several in preparation

Jiang, F., Y.-L. Hsieh, Rice Straw Nanocelluloses: Process-linked Structures, Properties and Self-assembling into Ultra-fine Fibers, in ACS Symposium Series Book: "Nano-celluloses, their Preparation, Properties, and Applications", in press.

Jiang, F., D.M. Dinh, Y.-L. Hsieh, Adsorption and desorption of cationic malachite green dye on cellulose nanofibril aerogels, , *Carbohydrate Polymers*, 173: 286-294 (2017).

Jiang, F., Y.-L. Hsieh, Cellulose nanofibril aerogels: synergistic improvement of hydrophobicity, strength, thermal stability via crosslinking with diisocyanate, ACS Applied Materials & Interfaces, *9* (3), 2825–2834 (2017).

Gu, Jin and Y.-L. Hsieh, Alkaline cellulose nanofibrils from streamlined alkali treated rice straw, ACS Sustainable Chemistry & Engineering, 5: 1730-1737 (2017).

PRESENTATIONS: 9

Hsieh, Y.-L., Functional nanofibers and hierarchical hybrids, **invited,** Universitat Politècnica de Catalunya- Barcelona, Polytechnic University of Catalonia, Barcelona, Spain, February 22, 2017.

Fukuda, J., Hsieh, Y.-L., One pot generation of hydrophobic nanocellulose by a multi-functional butadiene sulfone (BDS), Division of Cellulose and Renewable Materials, ACS National Meeting, San Francisco, CA, April 2-6, 2017.

Hsieh, Y.-L., Single-sourced nanocelluloses: process-linked characteristics and behaviors, **Invited**, Symposium in honor of Dr. Rajai Atalla, Division of Cellulose and Renewable Materials, ACS National Meeting, San Francisco, CA, April 2-6, 2017.

Hsieh, Y.-L., Strategies toward cellulose nanofibers, porous fibers and hybrids, Division of Cellulose and Renewable Materials, ACS National Meeting, San Francisco, CA, April 2-6, 2017.

Hsieh, Y.-L., F. Jiang, Cellulose aerogels via self-Assembling and electrospinning, Division of Cellulose and Renewable Materials, ACS National Meeting, San Francisco, CA, April 2-6, 2017.

Hsieh, Y.-L., Cellulose aerogels with tunable hydrophilicity-hydrophobicity via facile self-assembling, gelation and crosslinking, International Conference on Nanotechnology for Renewable Materials, Montreal, Quebec, Canada, June 5-8, 2017.

Hsieh, Y.-L., Cellulose aerogels with tunable amphiphilicity to hydrophobicity, **Invited**, International Conference on Natural Fibers (ICNF), Braga, Portugal, June 20-23, 2017.

Hsieh, Y.-L., Nanocelluloses with tunable amphiphilicity and functionality, Advances in Functional Materials, University of California, Los Angeles, August 14-17, 2017.

Hsieh, Y.-L., Green processes for functional nanocelluloses, **Invited**, International Cellulose Conference, Fukuoka, Japan, October 17-20, 2017.