Powder cellulose nanocrystal (nanowhisker) prepared for functional filler of polymers

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Toshihiko Arita (Tohoku Univ.) and

Jun Araki (Shinshu Univ.)

tarita@tagen.tohoku.ac.jp

jun@shinshu-u.ac.jp

Background

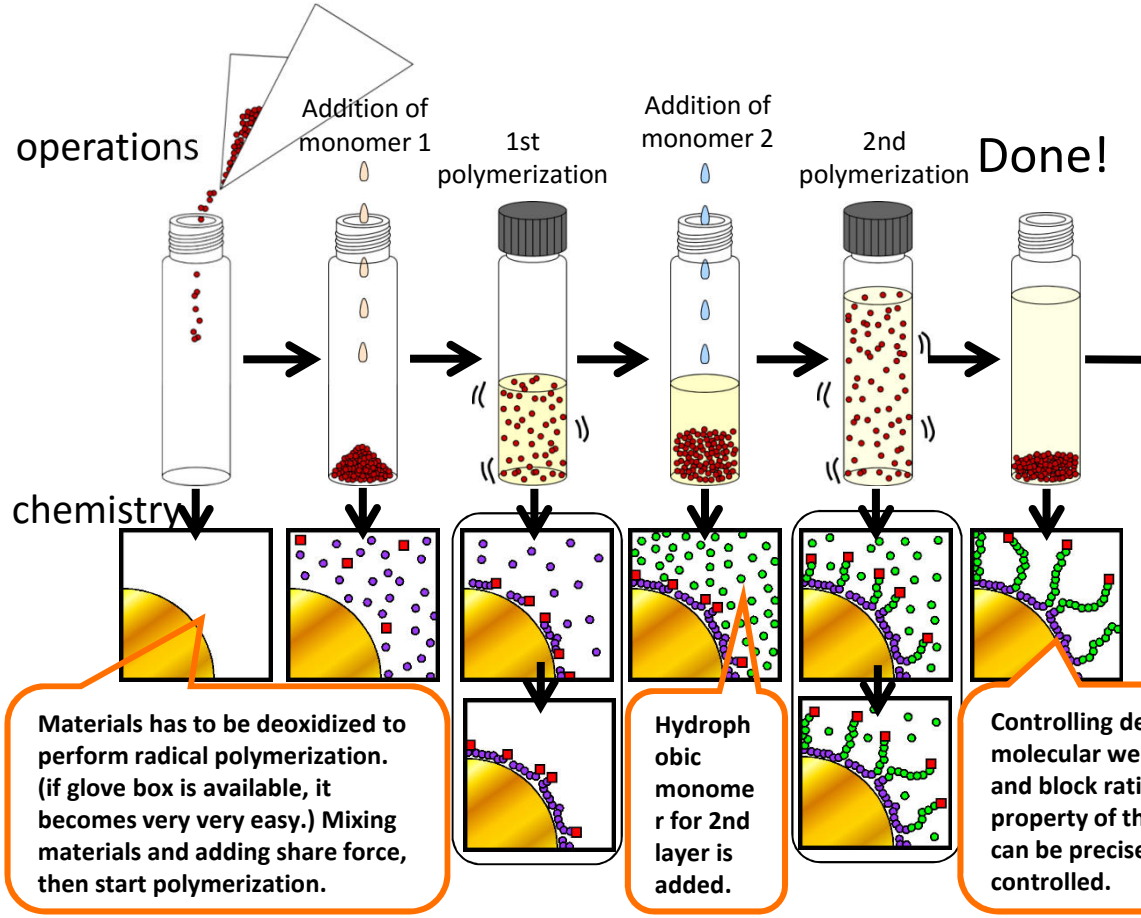
- Most of conventional polymeric materials include fillers,



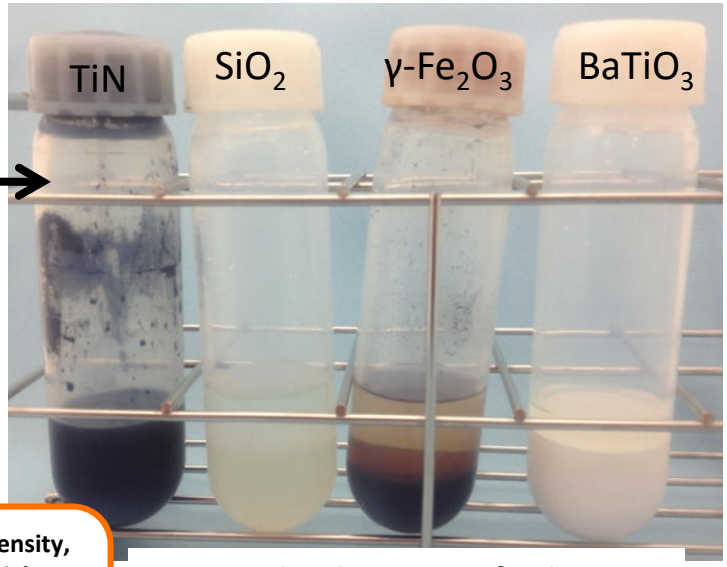
- very good dispersion in polymer matrix is required for the sake of effective reinforcement effect.
- In the case of elastomer (rubber), fillers also have to lead reinforcement functions, not only dispersion but connection (reaction) between filler and polymer should be considered.
- A lot of types of surface control, those are important!

Polymerization with Particle (PwP)

Controlled Radical Polymerization with Particles (CRPwP)



Grams of fillers can be treated in a 50 mL PFA Bottles



It need only 10 mL of solvent. 5 orders of magnitude larger efficiency than conventional methods

- ✓witout choosing material of fillers, polymer-functionalized filler can be made by the method.
- ✓quite stable polymer-functionalized particles by only one pot synthesis and operated with very high- concentration and yield!!

Benefits of cellulose based material

Inorganic fillers including nanoparticle have been successful, however

For further performance and functionality,

- Stronger but lighter material
- Transparent filler
- Unique (aspect ratio)
- Carbon neutral
- Economy

Nano celluloses density：~1,5 g/cm^3

good physical properties of nanowhisker (modulus:150 GPa, strength at break: 6 GPa §) → like alamido fiber（Kevlar®）

1．Cellulose nanofiber（CNF）

Width:4～100nm, length: more than 5μm very large aspect ratio, made by mechanistic fibrillation

2．Cellulose nanocrystal（CNC）(cellulose nanowhisker（CNW）)

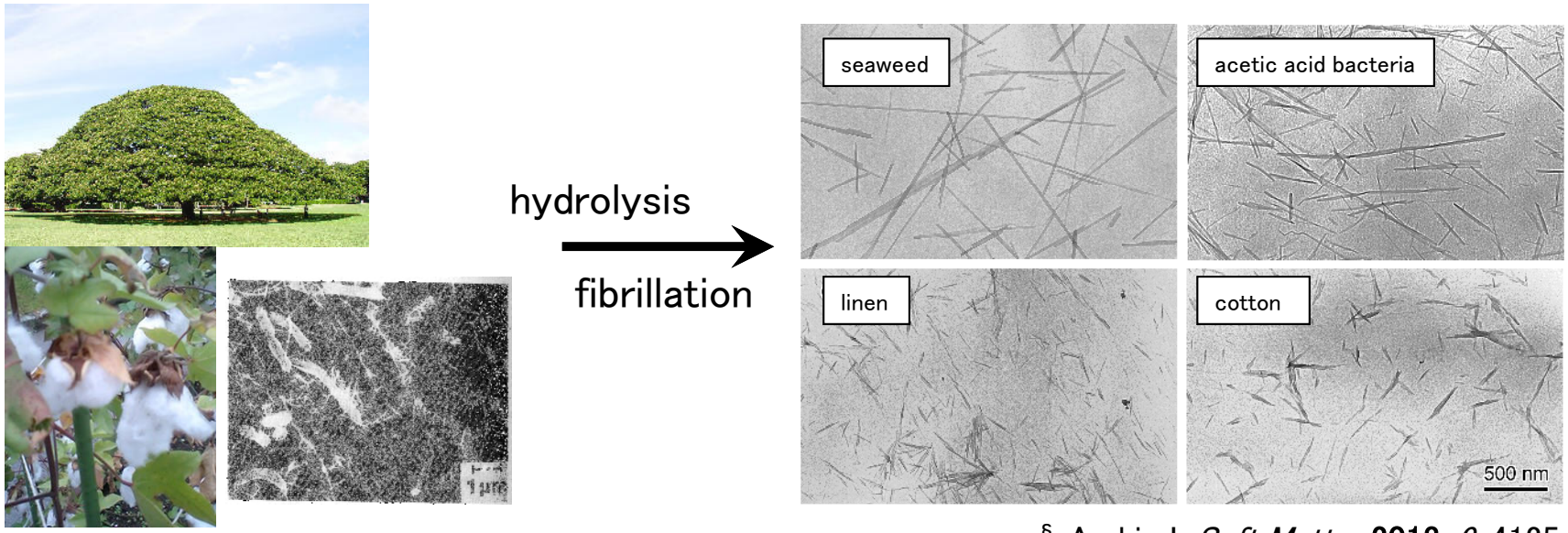
Needle like crystal width:10～50nm, length:100～500nm
Made by fibrillation after acid catalyzed hydrolysis

§ Saito, T.; Kuramae, R.; Wohlert, J.; Berglund, L. A.; Isogai, A. *Biomacromolecules* **2013**, *14*, 248−253.

Characteristic of cellulose nanocrystal (whisker)

"cellulose nanowhisker"

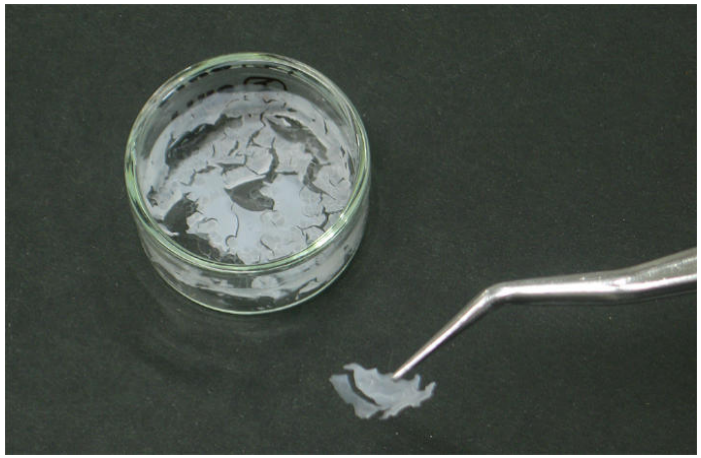
- Rod-shaped colloidal particle made by acid catalyzed hydrolysis and fibrillation of natural cellulose
- 2∽20 nm width, 0.1∽several μm length (size is dependent on plant species)
- Shows liquid crystallinity. Applications are mainly depends upon fillers
- Mostly, production is depending on grinding in aqueous solution after acid catalyzed hydrolysis.



§ Araki, J. *Soft Matter* **2013**, *9*, 4125–4141.

Objective = Locations of problems

- Aqueous nanowhiskers cause very strong keratinization (irreversible aggregation) on drying.
- Causal is hydrogen bonding between hydroxyl groups on the surface of cellulose.
- To maintain dispersion, drying process is contraindication (taboo), it has to be stored in aqueous dispersion.



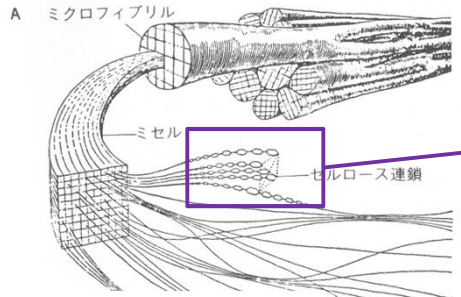
Keratinized cellulose nanowhiskers
(irreversible aggregation)

Simply, it is very hard to handle in current form.

We have studied an new method to prepare “powder” cellulose nanocrystal.

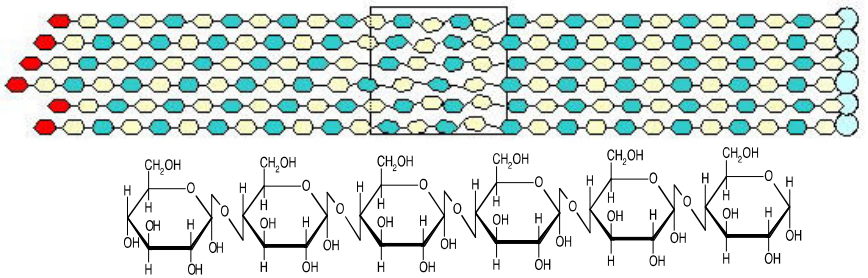
Nobel root for “powder” cellulose nanowhisker

特願2015-107801



Bonner, J.; Galston, A. W. Principles of Plant Physiology, W. H. Freeman & Co., 1952.

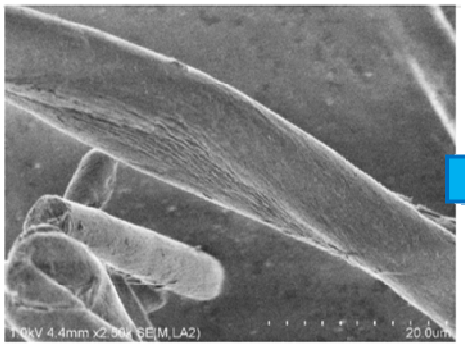
amorphous



Recipe for cellulose nanocrystal

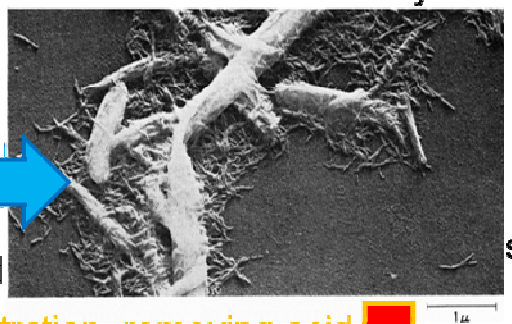
operation in ➡: water (practical) ➡: organic solvents (new)

Cellulose microfibril



Treatment by dilute inorganic acid

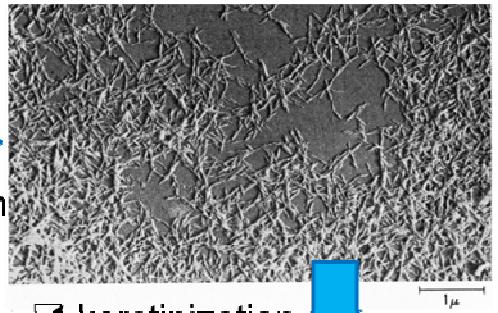
Cellulose microcrystal



Filtration, removing acid

grinding separation

Crystalline cellulose (nanowhisker)



☑ keratinization

Newly developed “powder” cellulose nanocrystal

Switching solvent from water to organic solvent after filteration, then subsequent process was conducted in organic solvent.

- ✓ inhibit keratinization by reducing cohesive force (capillary force).
- ✓ easy transfer to surface treatments (e.g., PwP) after grinding.
- ✓ high concentration and less drying therefore energy efficient
- ✓ utilize friction triboelectric charging in dielectric medium



☑Kept powdery state

Sample and method

- Raw material：cotton
- Boiling in 2.5 M HCl for 40min (hydrolysis) → water washing
- Centrifuge collection and solvent exchange to acetone → targeted organic solvents
  - Solvents：toluene・ cycrohexane・ ethylacetate・ dimethylacetamide・ acetonitrile
- Grinding by double blade rotary homogenizer（ POLYTRON PT2500E ）
  - concentration：2%、10%、20%
  - Grinding time：15min, 2hours
  - Rotational frequency：12000 rpm

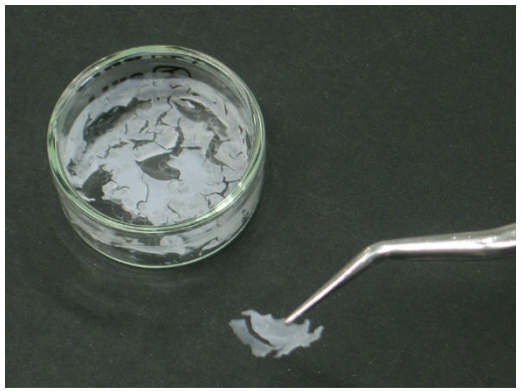


- Obtained slurry was dried
- Visual and SEM observations
- Dispersion in water （ 1%w/w ）was examined.

results　～ appearance of sample; keratinization～

水中粉砕物（粉砕時間15分）

- 懸濁液は白濁し、安定である
- 風乾により角質化、堅いフィルムを形成。水中に投入してもナノウィスカーレベルまで再分散しない



トルエン中粉砕物（粉砕時間2時間）

- 懸濁液は比較的早く沈降する（セルロースの比重1.59＞トルエンの比重0.87の差のためであり、凝集形成ではない）
- 風乾のみで極めて微細な粉末を形成する



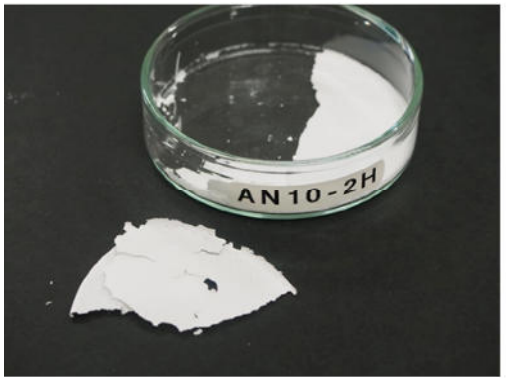
results ～ appearance of sample; keratinization～

- Appearance of dried cellulose samples after grinding



toluene





acetonitrile
(MeCN)



- Low dielectric solvents such as toluene and cyclohexane → fine powder
- High dielectric solvents such as MeCN and DMAc → keratinized film

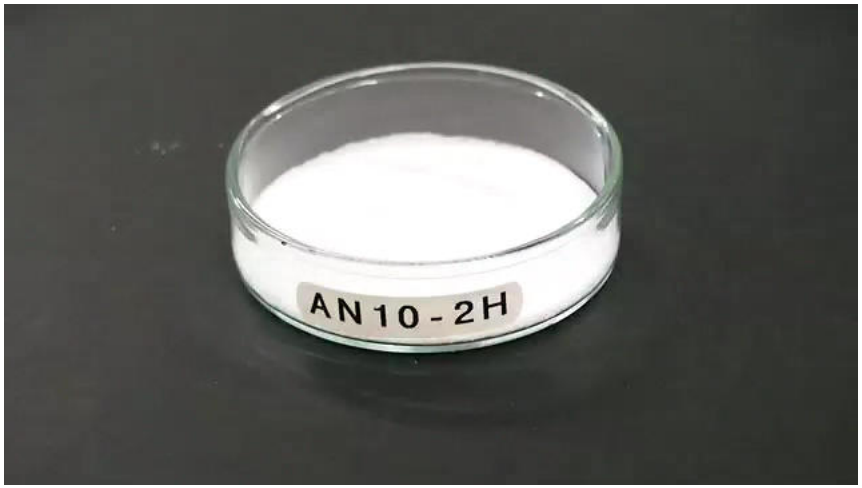
results ～ appearance of sample; keratinization～



TL10-2H（ground in toluene）

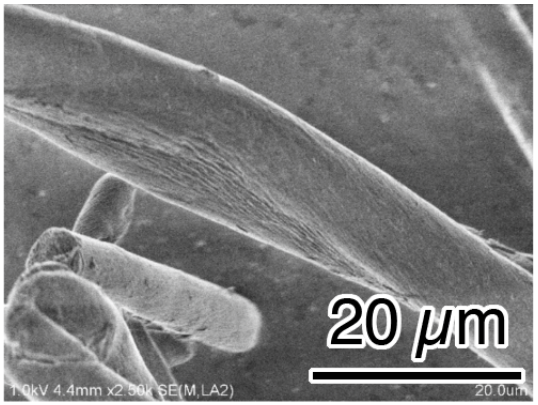


CY10-2H（ground in cyclohexane）

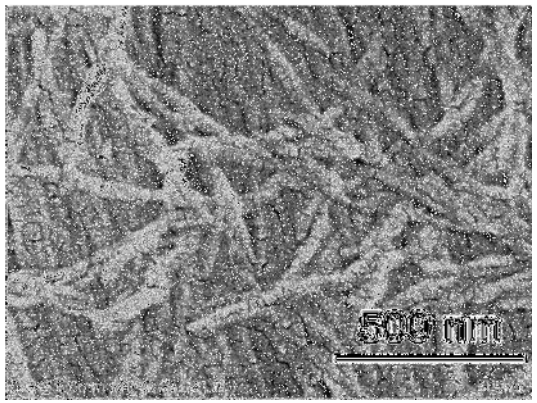


AN10-2H（ground in acetonitrile）

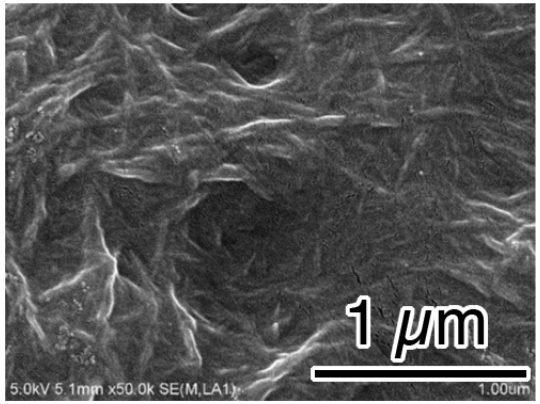
results ～SEM observation～



Before grinding



In toluene

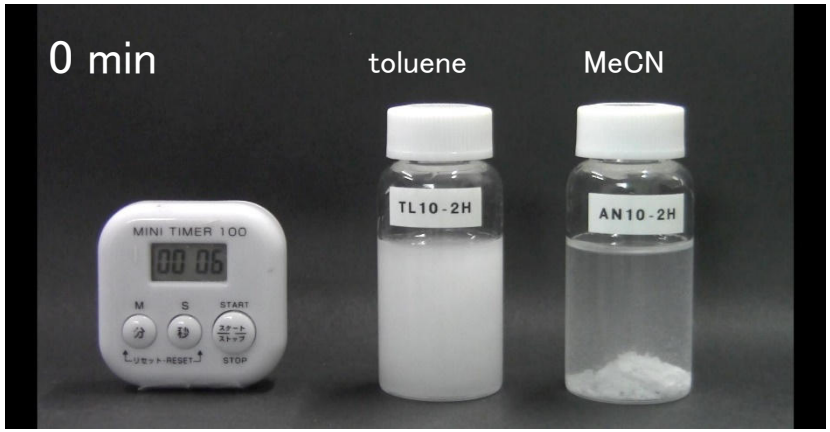


In DMAc

- Nanowhisker can be found in ground sample in toluene
- Plate like agglomeration (anastomoses between whiskers) has been seen in high dielectric solvent (DMAc, MeCN) → Keratinization

results ～redispersibility in water～

Dried powders from organic slurries were dispersed in water（1wt%）
Then, shaken and observed the settling behavior.







- Toluene ground sample showed dispersed whiskers even after 1hour
- MeCN ground sample showed very quick settling down

results ～redispersibility in water～

solvent	Concentration at grinding(w/v%) (w/v%)	Grinding time	keratinization[a]	redispersion[b]	
				visible	supernatant conc.,%
toluene	10	2h	A	A	0.133
cyclohexane	10	2h	A	A	0.108
ethylacetate	2	2h	B	A	0.108
MeCN	10	2h	C	C	0.034

a. A: fine powder, B: flake, C: hard film

b. A: flote after 60min., B: flote for 10min, C: settle down with in 10 min.
supernatant concentration was measured 10min after preparing 1% of ground and dried samples

- Ground sample in toluene and cyclohexane become fine powder and showed very good redispersion in water
- Ground sample in ethylacetate (also in MEK) did not show keratinization
- Ground sample in acetonitrile (also in DMAc) showed solid aggregation and, of course, no redispersion in water

Surface functionalization of obtained cellulose by polymers

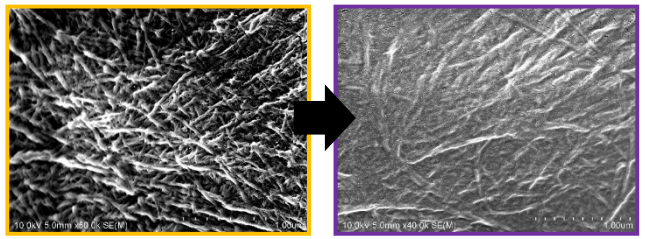
特願2014-19376, 特願2015-107801

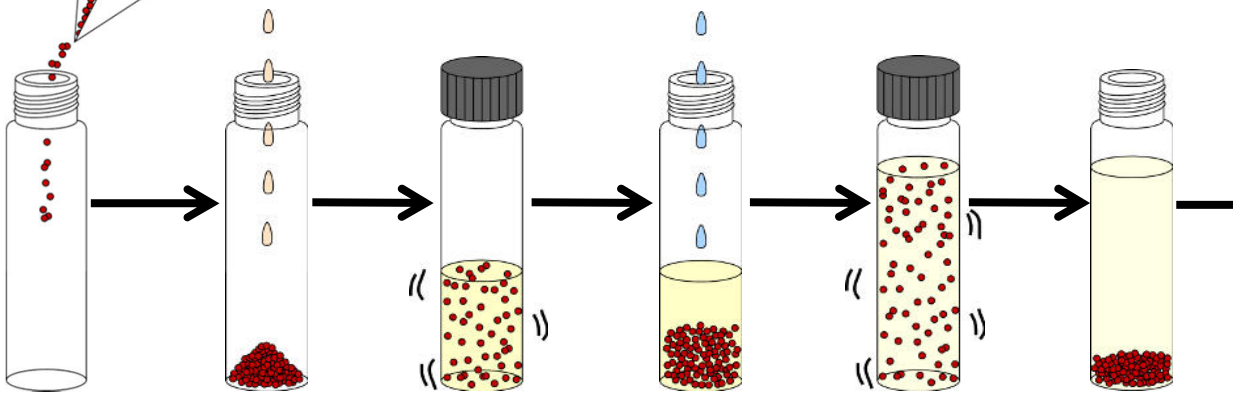
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Powder nanocellulose was used instead of inorganic particles

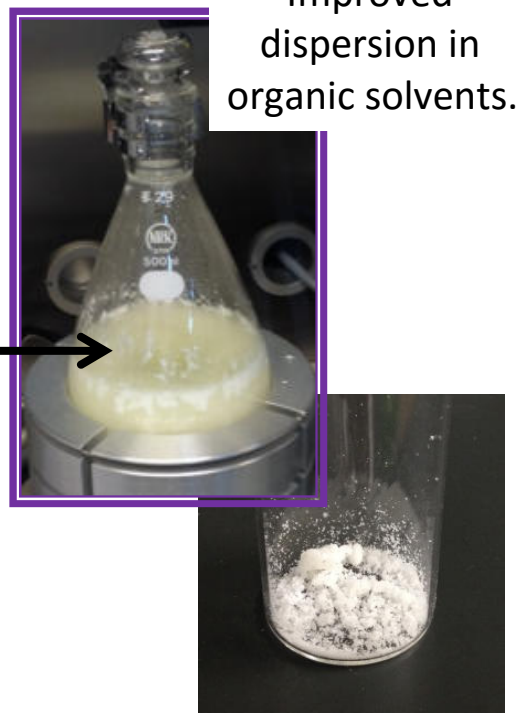


The surface of cellulose becomes smooth because of the polymer.





Improved dispersion in organic solvents.



After removal of solvents.

Arita, T. *Chem. Lett.* **2013**, *42*, 801–803.

Summary

- “Powder” cellulose nanocrystal (nanowhisker) without keratinization (irreversible aggregation) was successfully obtained by grinding acid catalyzed hydrolyzed cellulose in low dielectric organic solvents.
- Obtained powder actually includes nanowhiskers according to SEM observation.
- Extent of keratinization depends on dielectric constant of the solvent used. In lower dielectric solvents, it gives powder, instead in high dielectric solvents, it gives keratinized hard film.
- Obtained powder shows good redispersity in water.

Present status of our research

We are eager for partners who produces mass amount of powder cellulose nanowhiker!

THANK YOU FOR YOUR KIND ATTENTION!