Wet-TEM Investigation of Surface-Sulfated CNFs Dispersed in Water Gels

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Introduction

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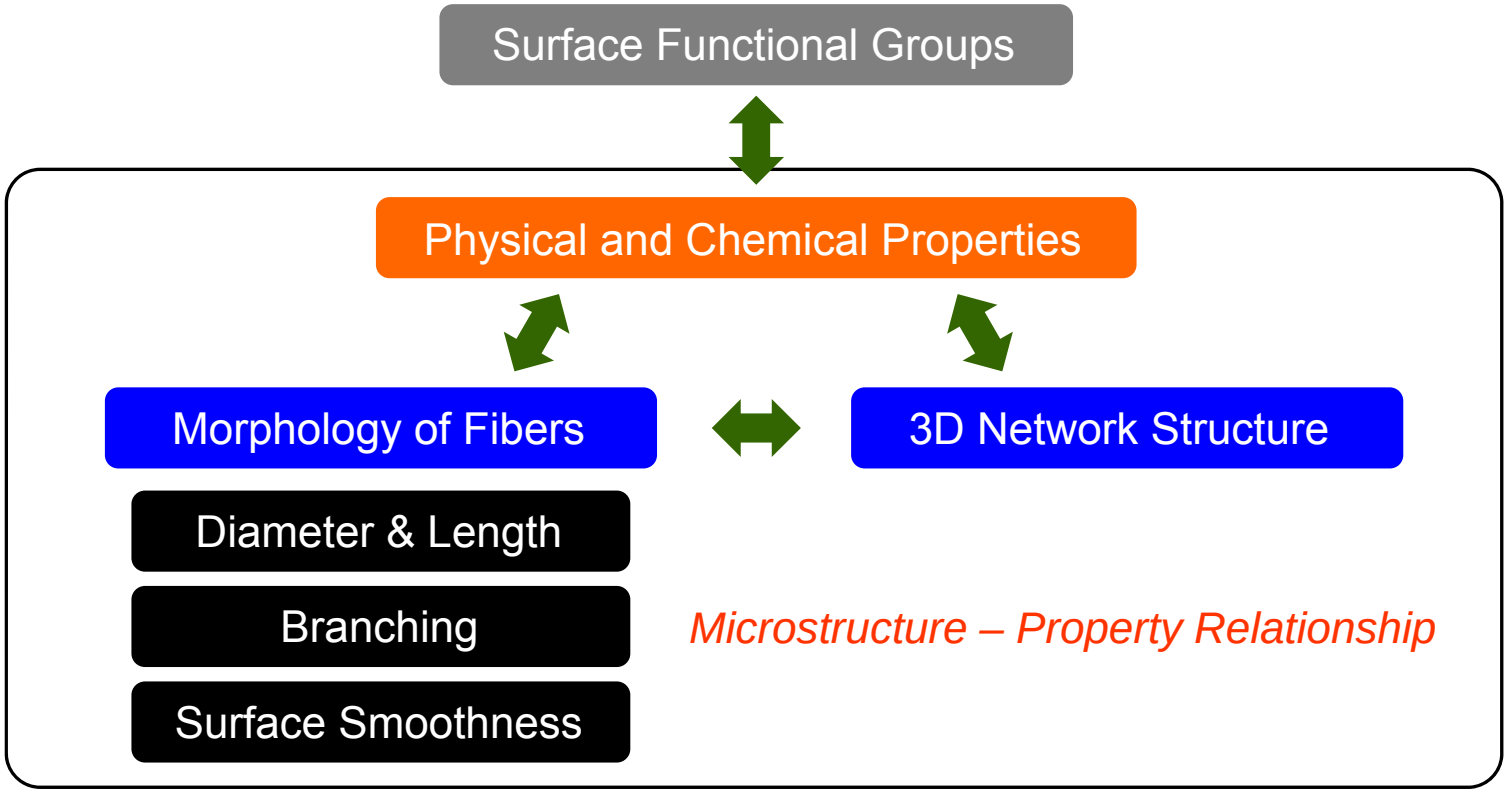
Factors Affecting to Physical and Chemical Properties of CNFs



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Preparation of Surface-Sulfated CNFs (S-CNFs)

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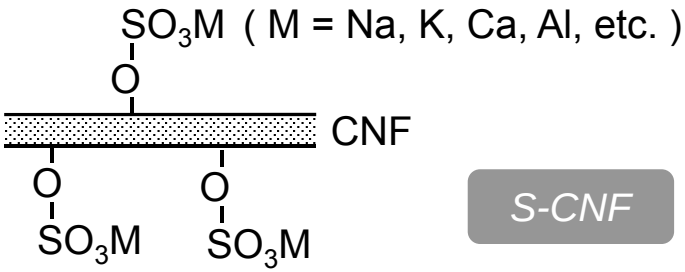
Mixing of reactants → Decantation → Stirring to form S-CNFs

Stirring
2 h at RT

Neutralization
Washing

- ▼ Pulp
- ▼ Sulfuric acid
- ▼ DMSO
- ▼ Acetic acid

▼ 5 min at RT



Specimen Preparation for TEM : Conventional Method

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0.2 wt% S-CNF Gel in Water

↓

Diluted with Distilled Water

↓

0.002 wt% S-CNF Gel in Water

↓

Dispersed on Carbon Films Supported by Microgrids

↓

Negatively Stained with Gadolinium Acetate

↓

Microstructure Investigation by TEM

(JEOL JEM-2100F Operating at 120 kV)

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Microstructure of S-CNFs Dispersed in Water

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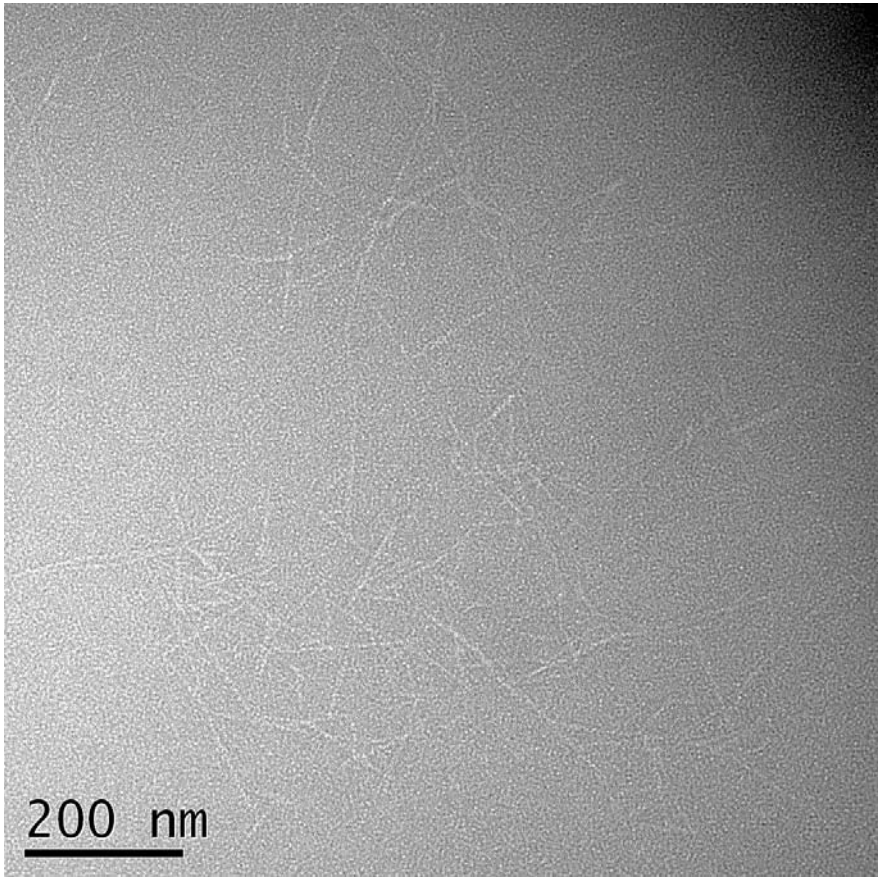

- Diameter 3 - 4 nm
- Length ~10^2 nm
- Curved or Bent

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Microstructure of S-CNFs Dispersed in Water

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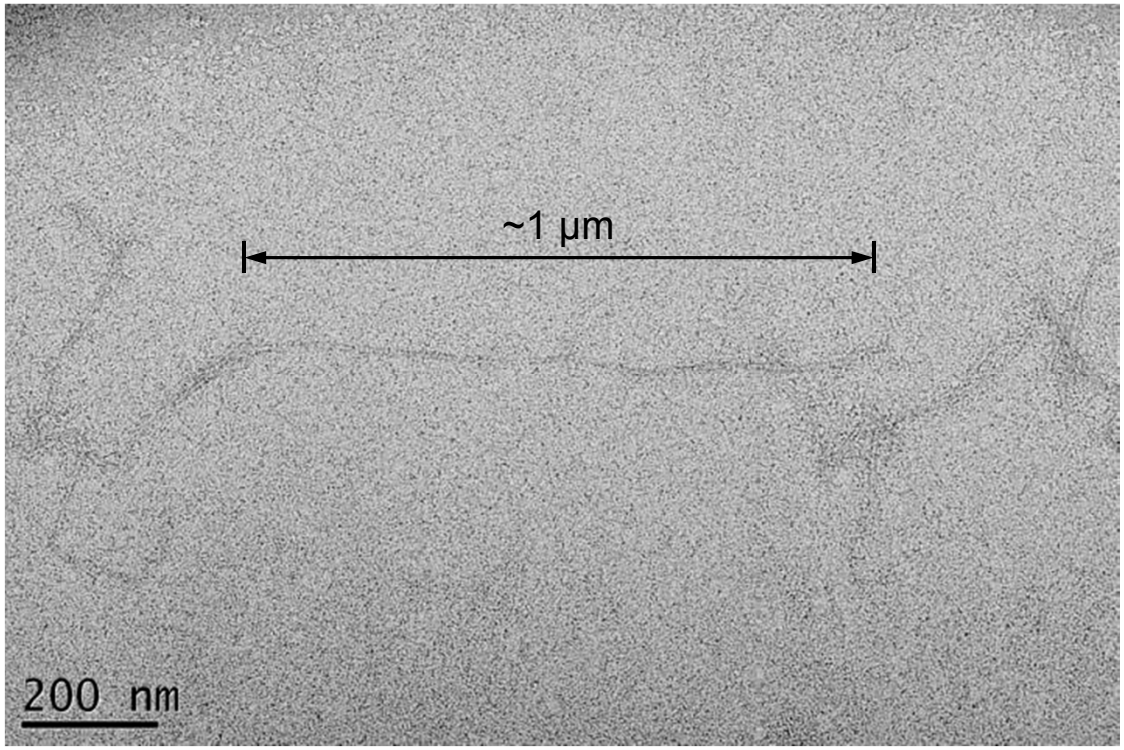

Long and slightly curved morphology of S-CNF

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Microstructure of S-CNFs Dispersed in Water

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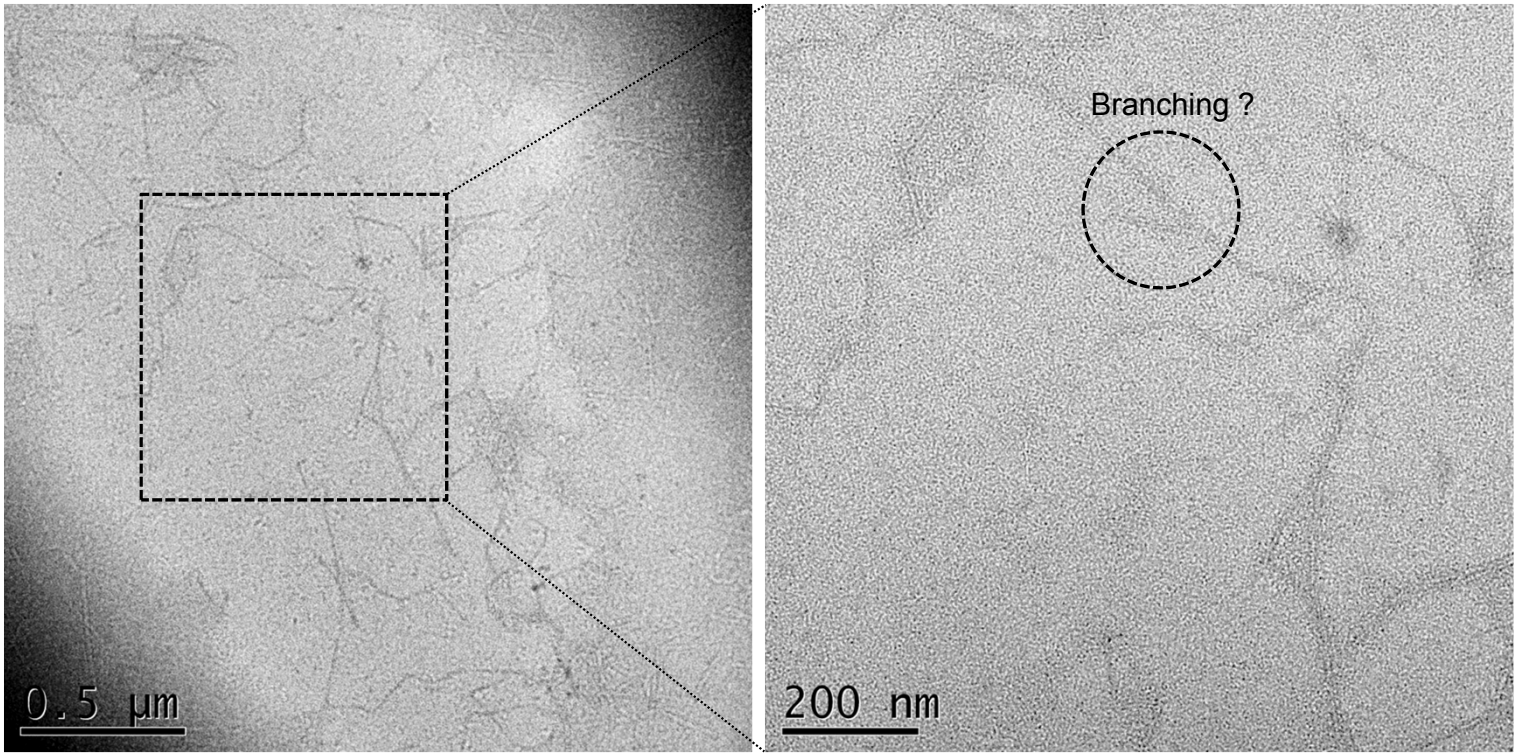

Branching of S-CNFs ?

Specimens for TEM Prepared by Conventional Method

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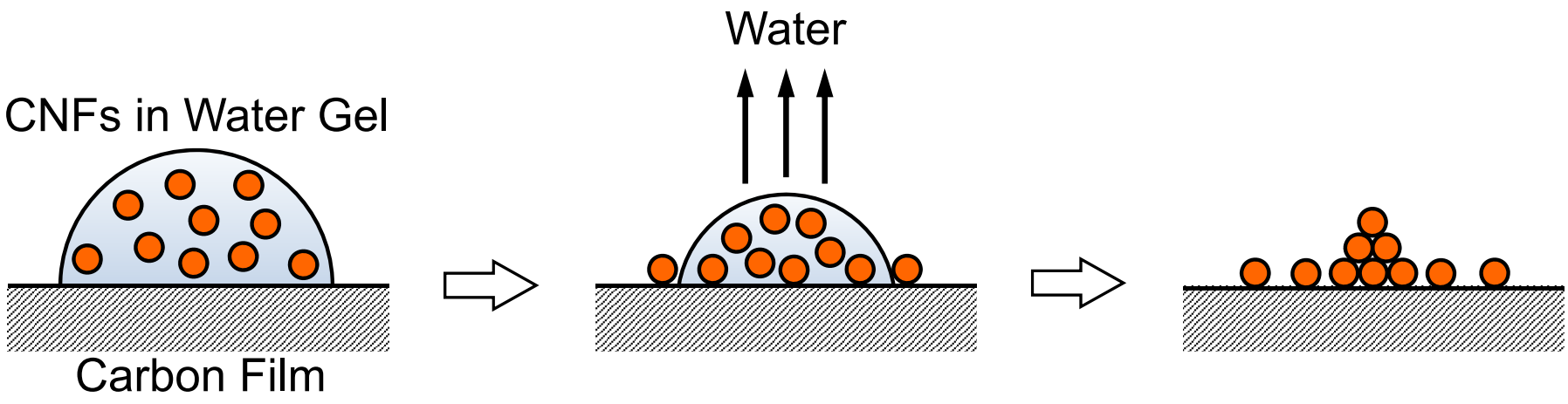

CNFs well dispersed

Water evaporated

CNFs aggregated and deformed
(Due to surface tension of water)

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Objectives of the Present Invesitigation

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Development of a novel technique of TEM investigation
to clarify the “real” structure of surface-sulfated CNFs (S-CNFs)
in Water Gel

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Wet-TEM Method
(to avoid aggregation and deformation of CNFs while specimen preparation)

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Specimen Preparation for Wet-TEM : Ionic Liquid

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Characteristics of Ionic Liquids

- Vapor Pressure ≈ 0 ➡ Almost no evaporation in vacuum
- Highly Hydrophilic ➡ Soluble in water、Replaceable with water
- Ionically Conductive ➡ Charge-up avoidable during TEM investigation

Suitable for Wet-TEM investigation !

Ionic Liquid for Electron Microscopy (Commercially Available)

HILEM IL1000 (Hitachi High Technologies)

Ethyl(2-hydroxyethyl)dimethylammonium Sulfonate $C_7H_{18}NO_4S$

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Specimen Preparation for Wet-TEM

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0.004 wt% S-CNF Gel in Water

↓

Mixed with Ionic Liquid

↓

0.002 wt% S-CNF Gel in Ionic Liquid + Water

↓

Dispersed on Carbon Films Supported by Microgrids

↓

Negatively Stained with Gadolinium Acetate

↓

Microstructure Investigation by TEM

(JEOL JEM-2100F Operating at 120 kV)

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Microstructure of S-CNFs Dispersed in Ionic Liquid

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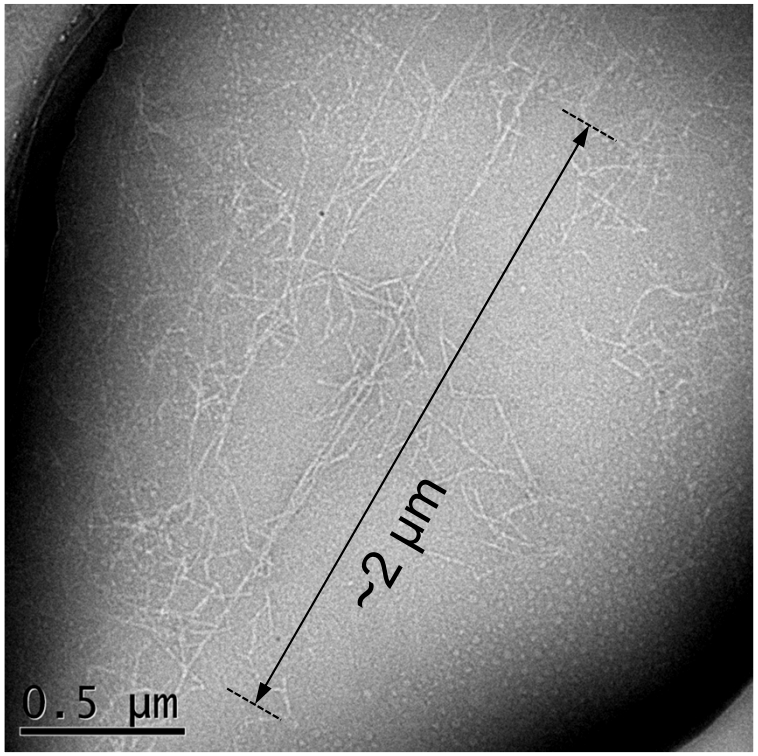

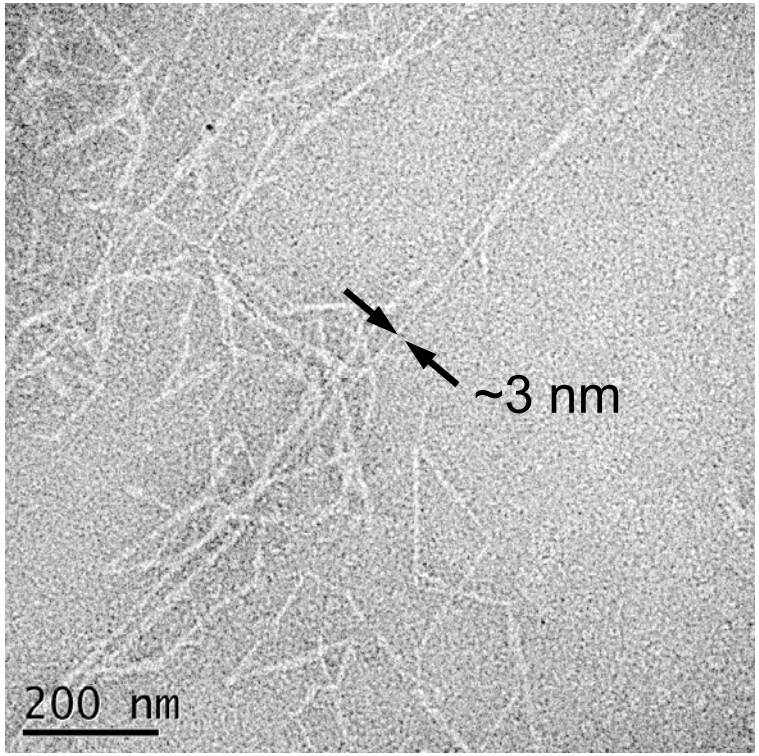

Long and straight morphology of S-CNFs

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Microstructure of S-CNFs Dispersed in Ionic Liquid

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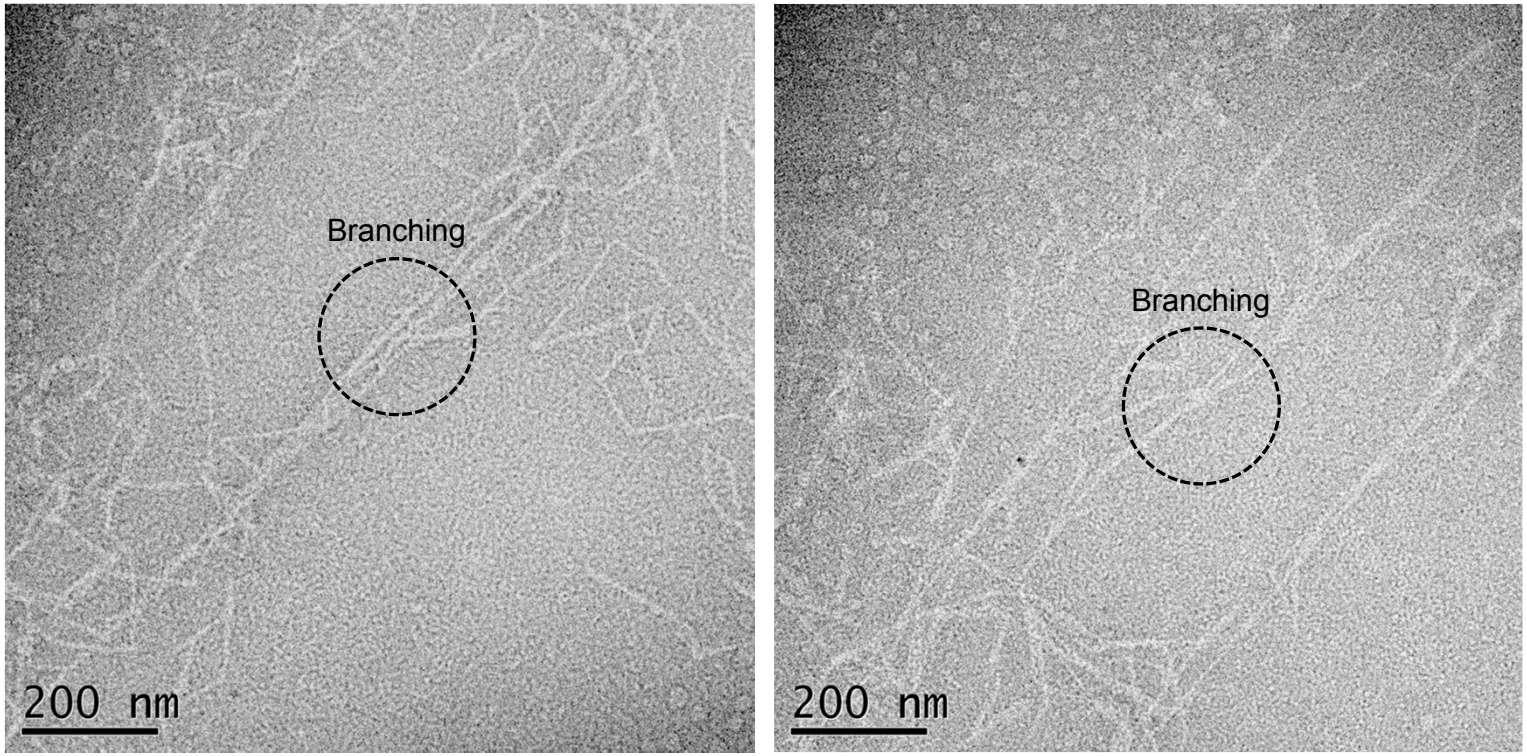

Branching of S-CNFs

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Conclusions

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We have developed a novel technique to investigate the microstructure of surface-sulfated cellulose nanofibers (S-CNFs) in wet conditions with ionic liquid and clarified the following features of S-CNFs.

- The diameter of single S-CNFs is around 3 nm.
- Some S-CNFs show a straight shape and their length is beyond 2 μm.
- Branching of fibers occurs at some points on S-CNFs.

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Thank you so much for your kind attention

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