Cellulose nanofiber nanocomposite for flexible and wireless electronics

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TAPPI NANO DIVISION

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CONTENTS

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CHAPTER

01 Introduction of KIMS

KIMS (Korea Institute of Materials Science)

nst National Research Council of Science & Technology

Purpose of Establishment

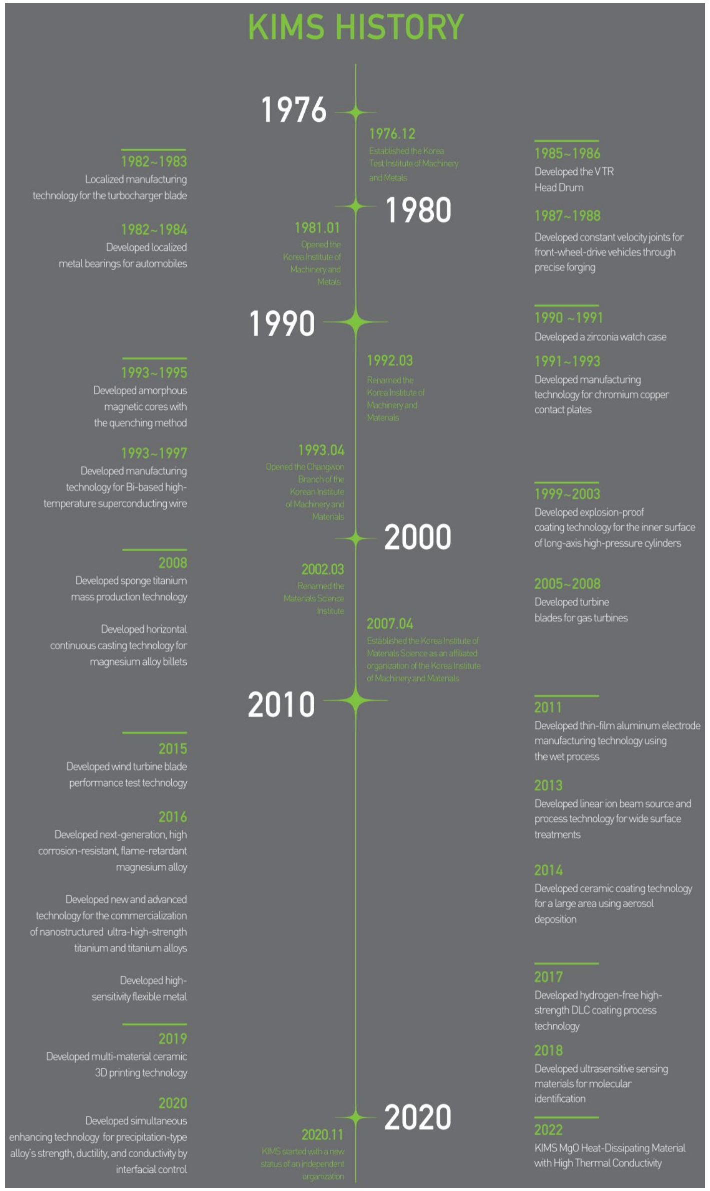
To support national research projects and policies and lead the development of the knowledge industry through supporting, fostering, and systematically managing Government-funded Research Institutes (hereinafter, "GRIs") in the field of science and technology

Government-funded Research Institutes (GRIs) under the NST

We would like to introduce our 25 research instites

KIST Korea Institute of Science and Technology	GREEN TECHNOLOGY CENTER	KBSI KOREA BASIC SCIENCE INSTITUTE	KASI Korea Astronomy and Space Science Institute	KISTI Korea Institute of Science and Technology Information
KIOM	KRIBB Korea Research Institute of Bioscience & Biotechnology	KITECH	ETRI Electronics and Telecommunications Research Institute	NSR
KICT Korea Institute of Civil Engineering and Building Technology	KRRI Korea Railroad Research Institute	KRISS	KFRI Korea Food Research Institute	WiKim World Institute of Kimchi
KIGAM Korea Institute of Geoscience and Mineral Resources	KIMM Korea Institute of Machinery & Materials	KARI Korea Aerospace Research Institute	한국에너지기술연구원 Korea Institute of Energy Research	KERI Korea Electrotechnology Research Institute
KRICT Korea Research Institute of Chemical Technology	KIT Korea Institute of Toxicology	KAERI Korea Atomic Energy Research Institute	KIMS Korea Institute of Materials Science	KFE Korea Institute of Fusion Energy

KIMS (Korea Institute of Materials Science)



As a government funded research institute, our objective at KIMS is to comprehensively facilitate R&D, test and evaluation and provide technical support related to materials technology in order to promote innovative technology and industrial development.

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CHAPTER

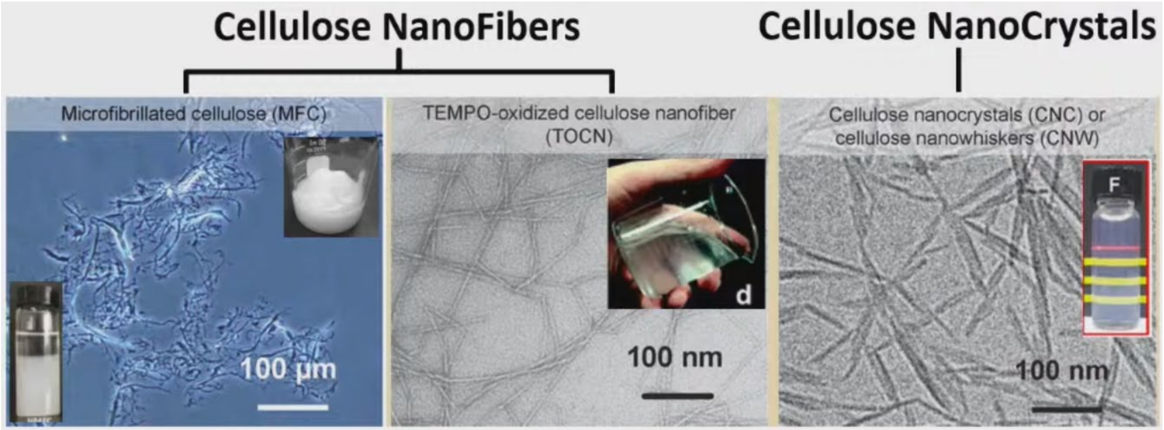
02 Nanofibrillation of Cellulose

Cellulose

Cellulose nanomaterials at KIMS



-Lumber
-Cotton
-Lyocell



-MFC
-TOCNF
-CNC

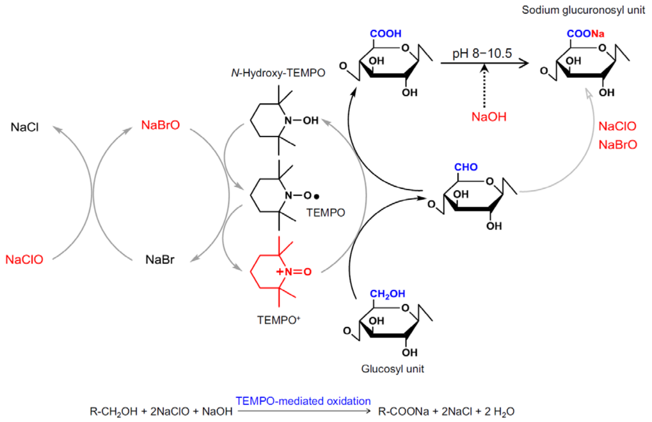
MFC	TOCNF	CNC
Morpholgy		
Uneven width of 10-2000 nm forming bundles	Uniform width 3~5 nm, several um in length	Uneven width of 5-10 nm, < 300 nm in length
Energy consumption in nano-conversion		
<700~1400 MJ kg^{-1}	<7 MJ kg^{-1}	<7 MJ kg^{-1}

- Fabrication of MFC, TOCNF by using pulp, cotton, and lyocell
- CNC fabrication by using cotton

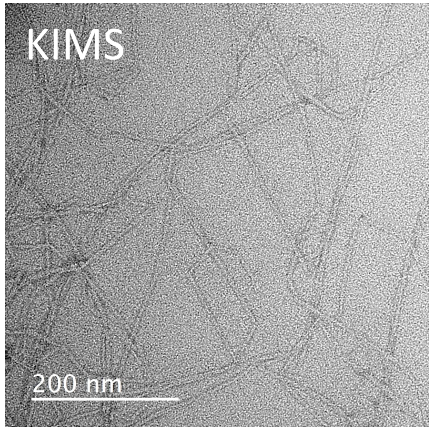
KIMS CNF

CNF fabrication and morphology

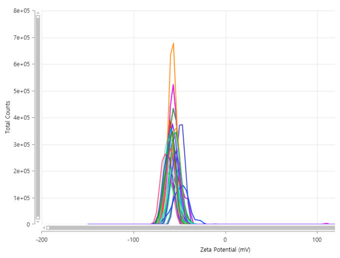
Several mm scale fiber



Current Opinion in Green and Sustainable Chemistry 2018, 12:15–21



TEM image

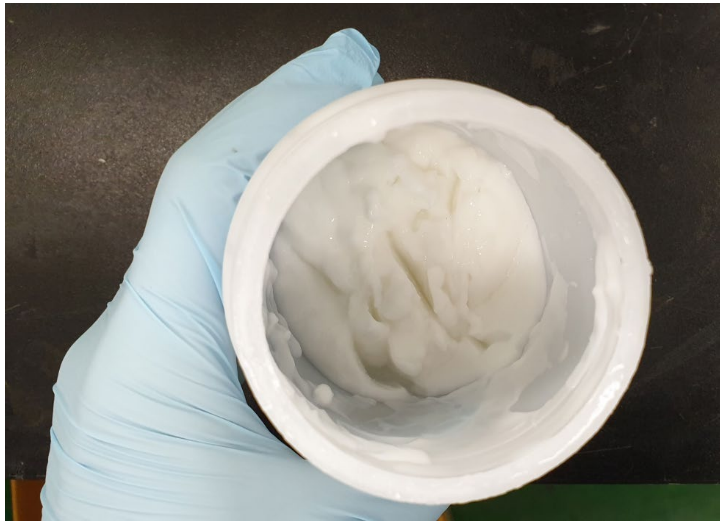


Zeta potential result

- TEMPO catalyst is introduced to produce TOCNF through electrostatic repulsive force through substitution of COO- functional groups on the surface of CNF
- Manufacture CNF by the high-pressure homogenizer equipment
- Similar CNF morphology to other references
- Width : 5 nm, length : several um
- Zeta potential : -56 ± 4.6 mV, Stably dispersed state

KIMS CNF

❖ CNF dispersion concentration control and aerogel fabrication



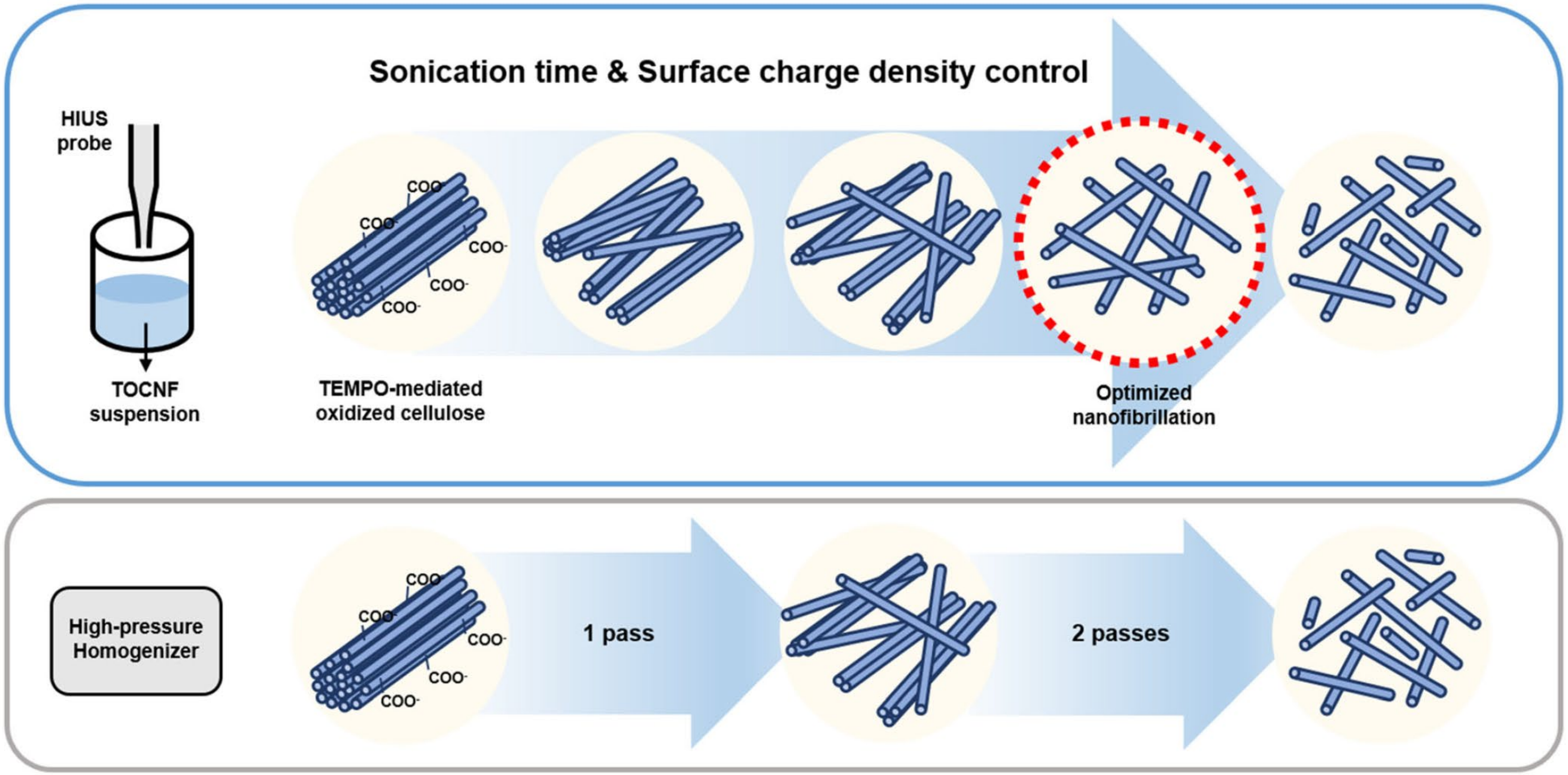
8 % CNF dispersion

1% dispersion and aerogel for composite

- High concentration dispersion for nanocomposite applications
- Aerogel or sponge for resin infusion process

Tracing the fibrillation of cellulose

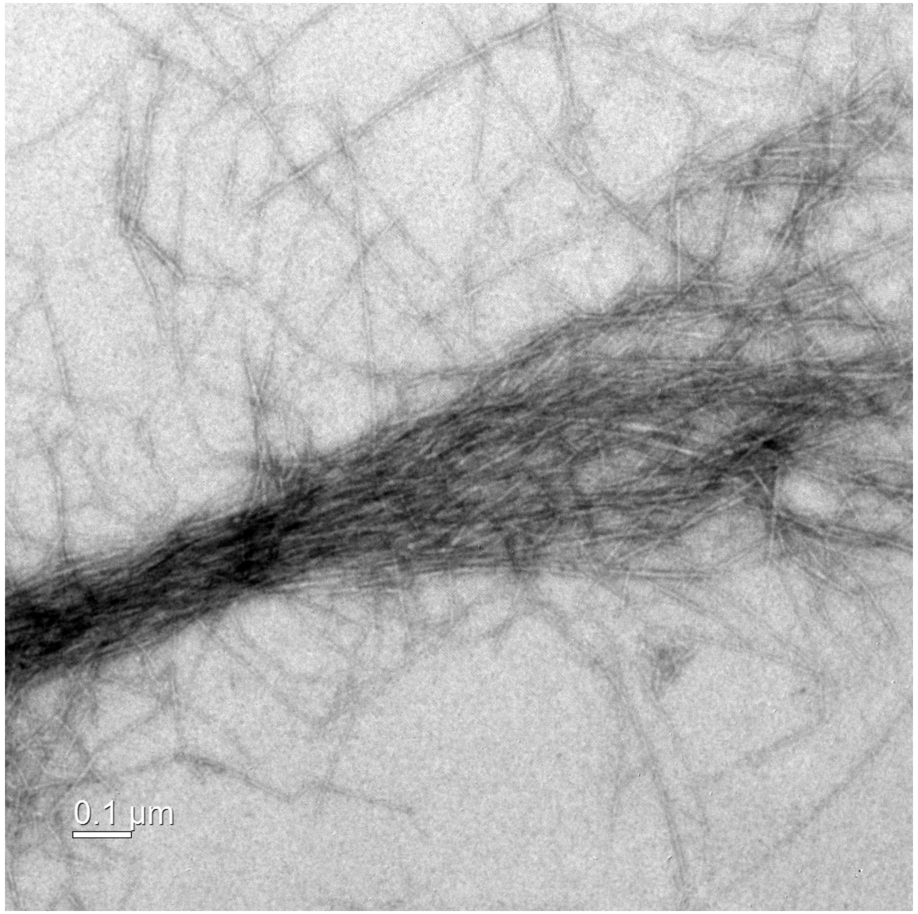
❖ Scheme of nanofibrillation by ultrasonication and homogenizer



Ref: Cellulose, https://doi.org/10.1007/s10570-020-03410-4, 2020, T.Park.

Nanofibrillation of cellulose

❖ Nanofibrillation process



Ref: Cellulose, https://doi.org/10.1007/s10570-020-03410-4, 2020, T.Park.

Morphology and rheological property of CNF

❖ Fibrillation tracing and modulus comparison

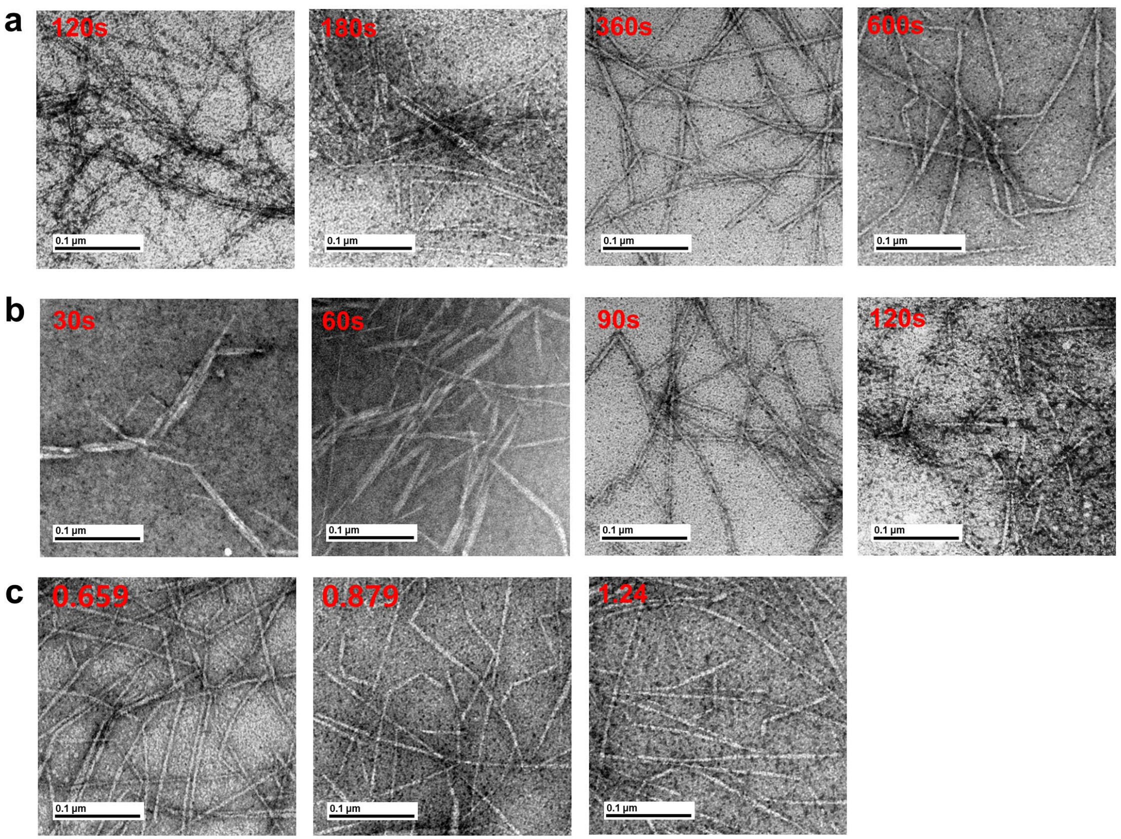


Fig. TEM images of TOCNF nanofibrillated using (a, b) high-intensity ultrasonication with surface charge density of (a) 0.879 and (b) 1.24 mmol/g and (c) high-pressure homogenizer with different surface charge densities.

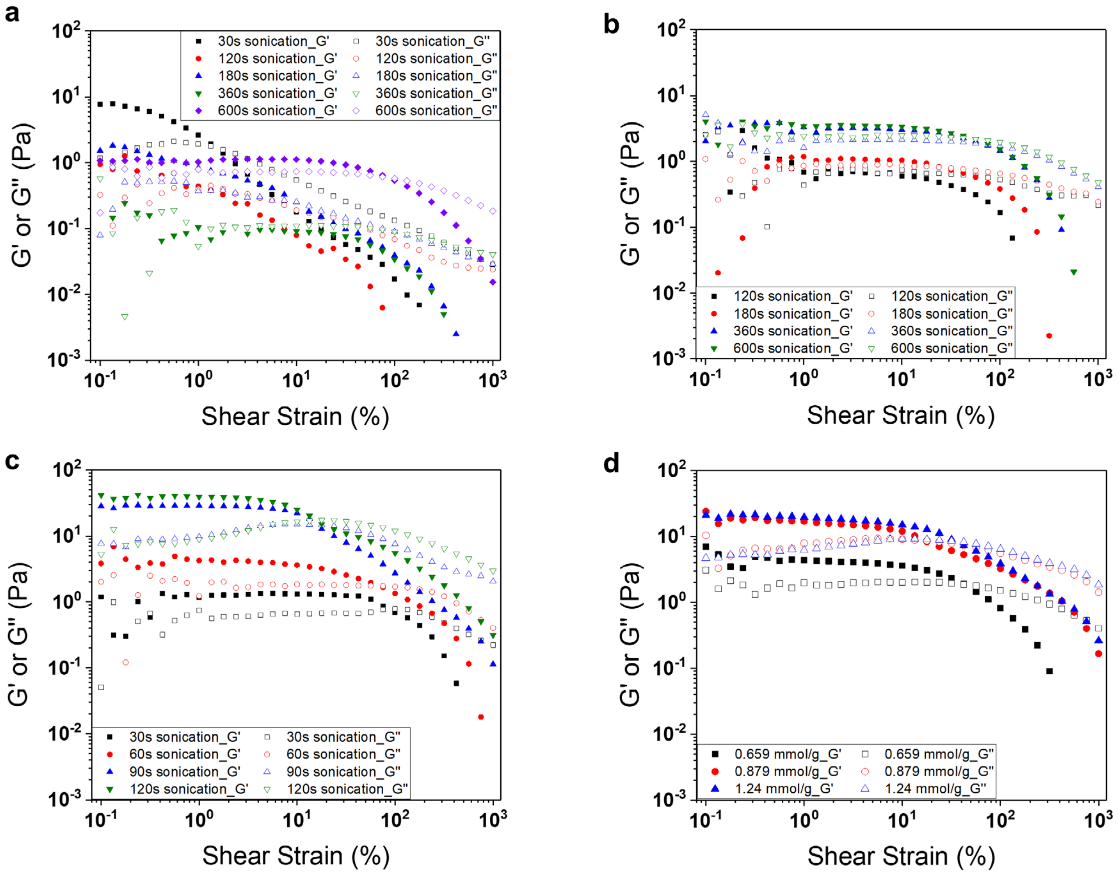


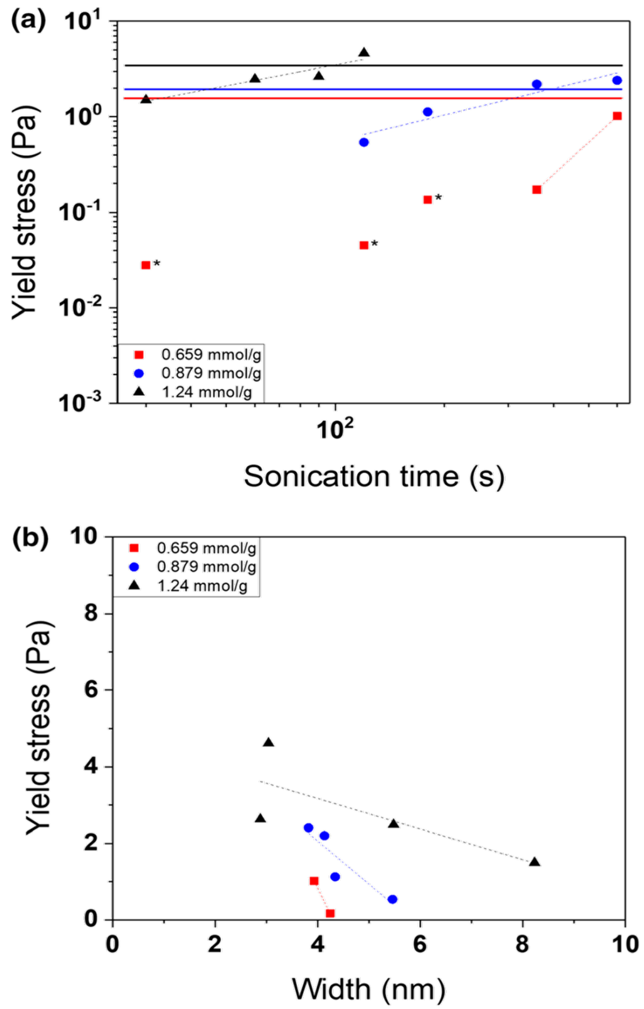
Fig. Oscillatory strain sweep measurement for 0.5 % TOCNF suspensions disintegrated by (a-c) HIUS and (d) high-pressure homogenizer with different surface charge densities

Degree of nanofibrillation prediction method

❖ Development of modeling that traces back the fibrillation process from the perspective of rheology

Table 1 Average width of TOCNF with different nanofibrillation methods and surface charge densities

Surface charge density (mmol/g cellulose)	Nanofibrillation method	Fibrillation time (s)	Avg. width (nm)	SD (nm)
0.659	HIUS	120	–	
		180	–	
		360	4.24	0.98
		600	3.93	0.98
	High-pressure homogenizer	–	3.86	0.93
0.879	HIUS	120	5.46	1.37
		180	4.34	1.51
		360	4.13	1.02
		600	3.82	1.07
	High-pressure homogenizer	–	3.84	1.10
1.24	HIUS	30	8.23	4.33
		60	5.48	1.39
		90	2.88	0.71
		120	3.04	0.80
	High-pressure homogenizer	–	3.20	0.67



→ Yield stress of 0.5 % TOCNF suspensions versus (a) sonication treatment time and (b) average width of the nanofibers as a function of surface charge densities. Solid lines indicate the yield stresses of TOCNF suspensions individualized using high-pressure homogenizer with different surface charge densities. (red: 0.659, blue: 0.879, and black: 1.24 mmol/g)

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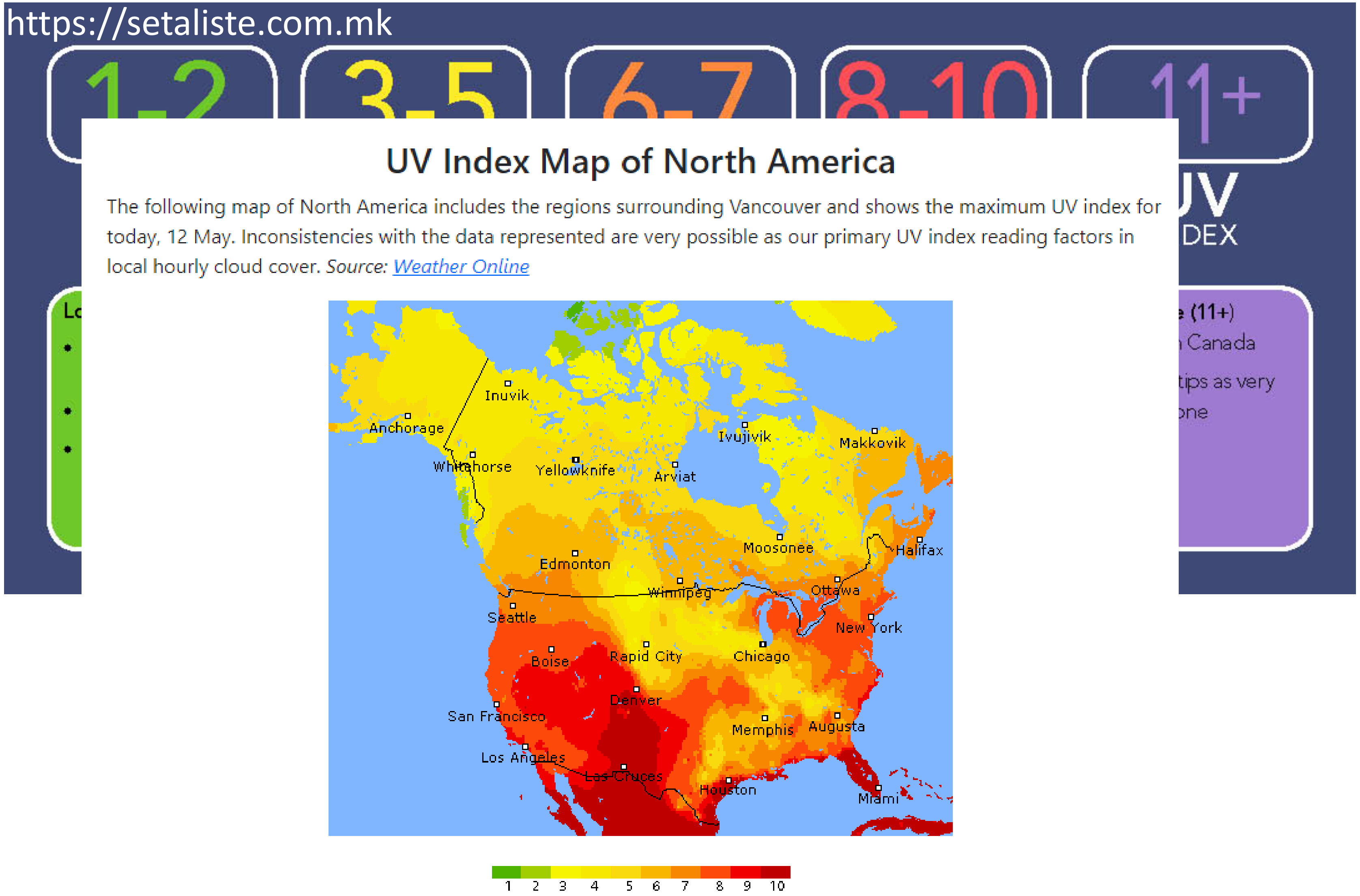
03 Flexible electronic device application

CNF for sensor application



https://www.uvindex.app/vancouver

CNF for sensor application

Air pollution (ozone depletion)

↓

Ultraviolet (UV) light exposure on earth increase

↓

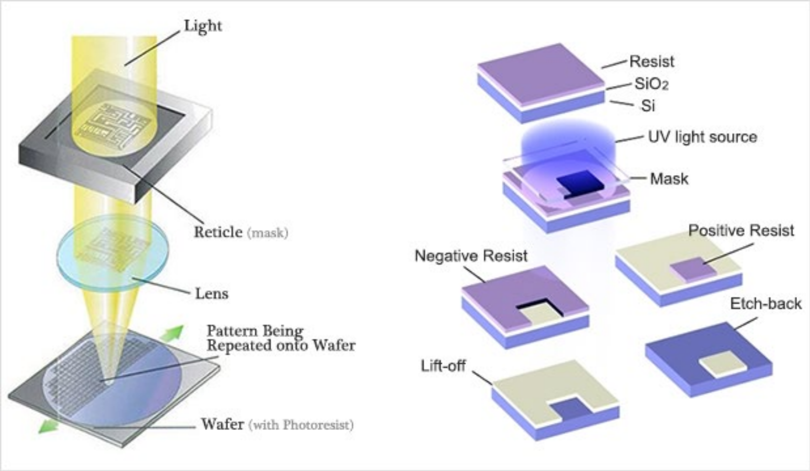
Causes harmful diseases (sunburn, skin cancer, cataracts)

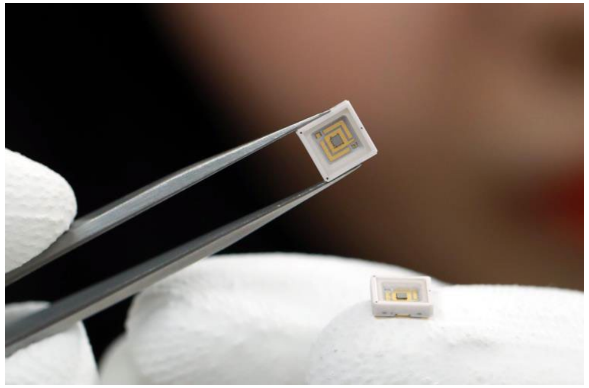
↓

Demands for evaluating the intensity of UV in day life

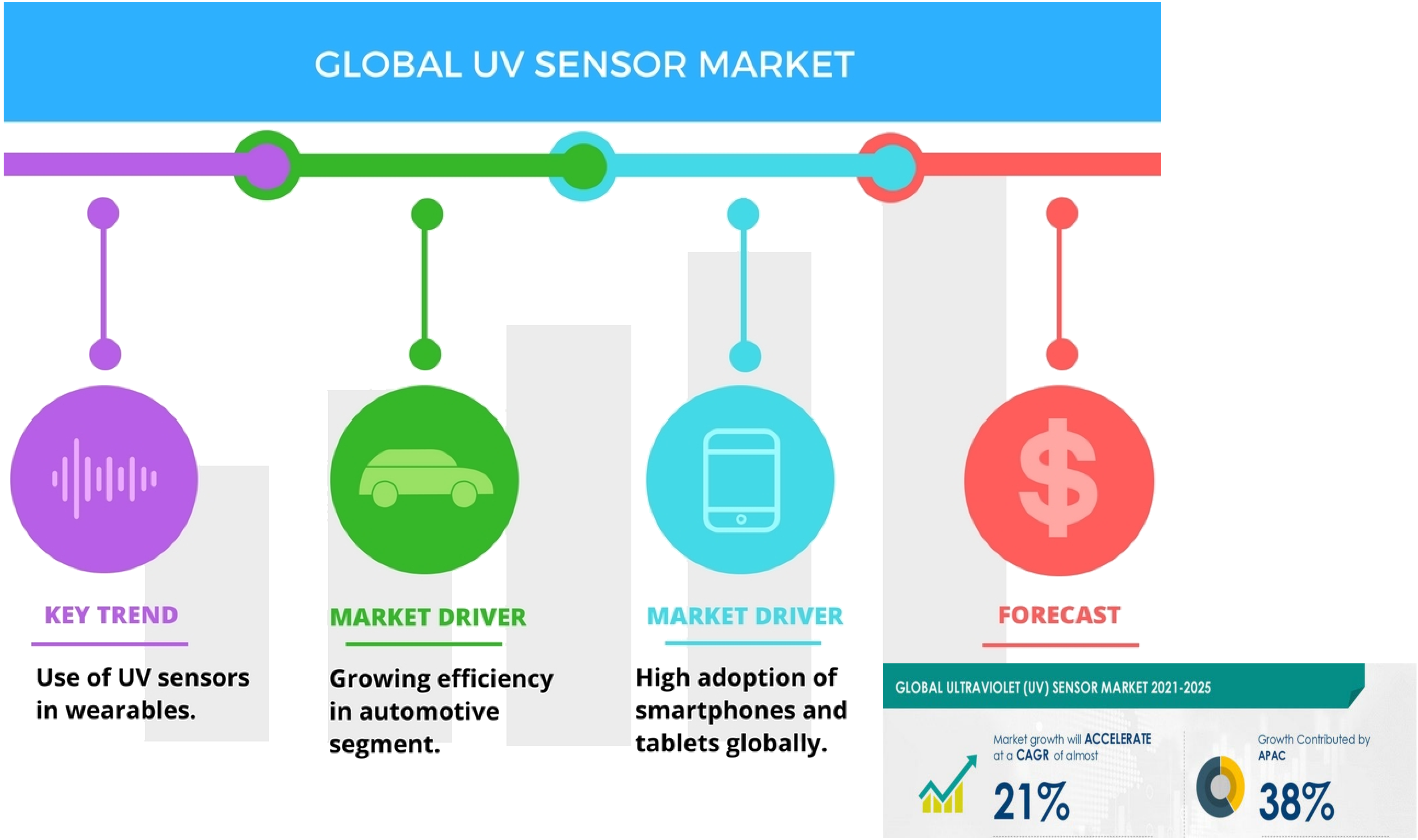
CNF for sensor application

❖ UV lamp applications



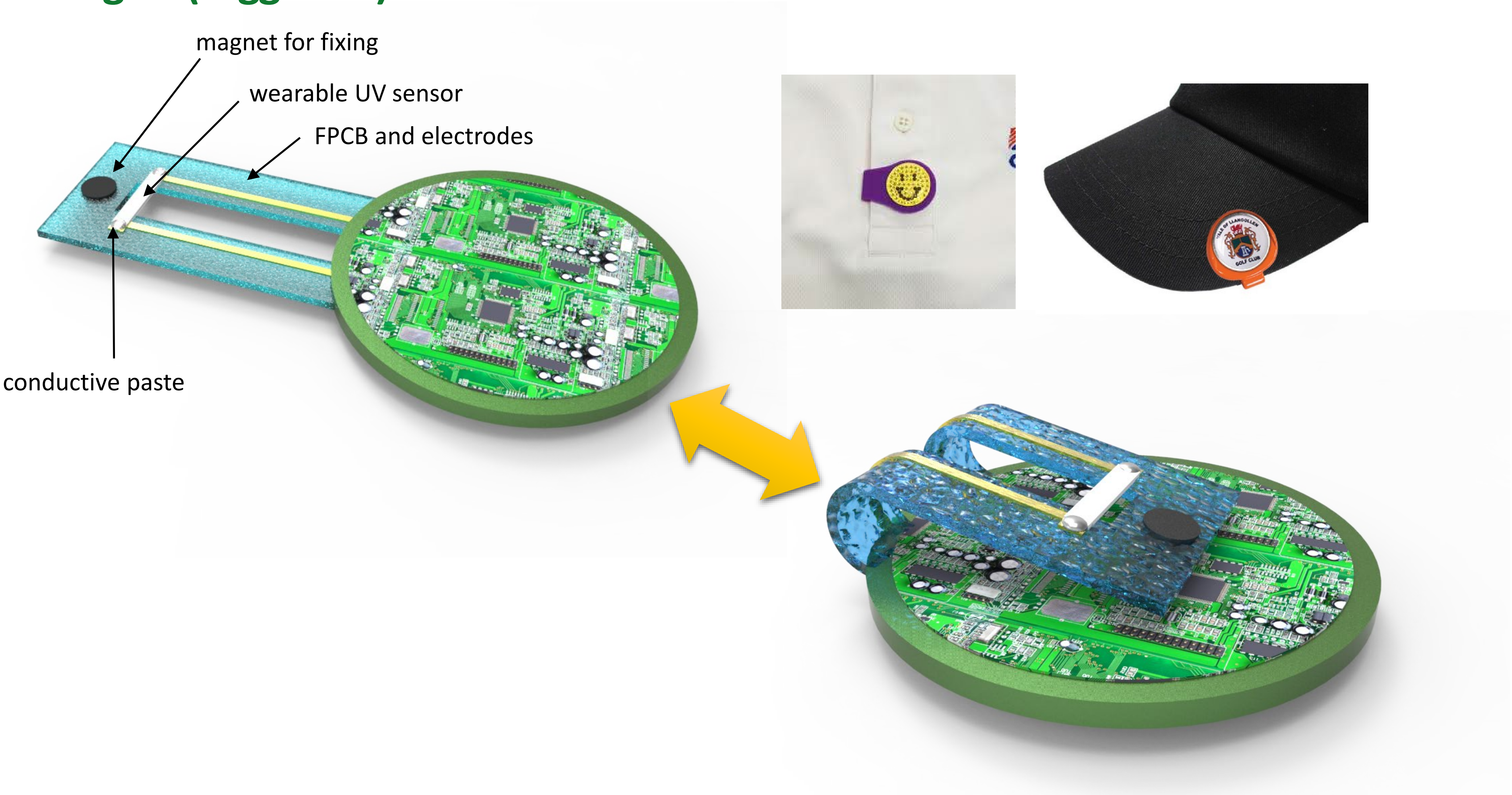


CNF for sensor application



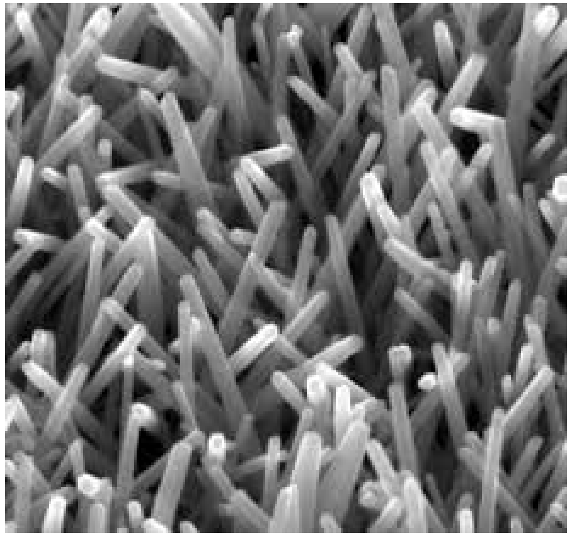
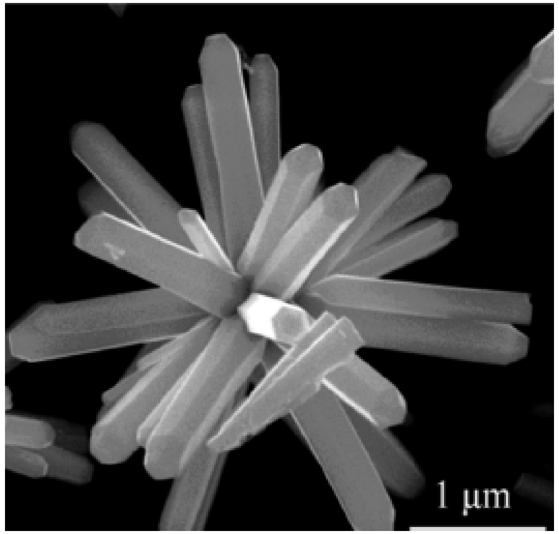
CNF for sensor application

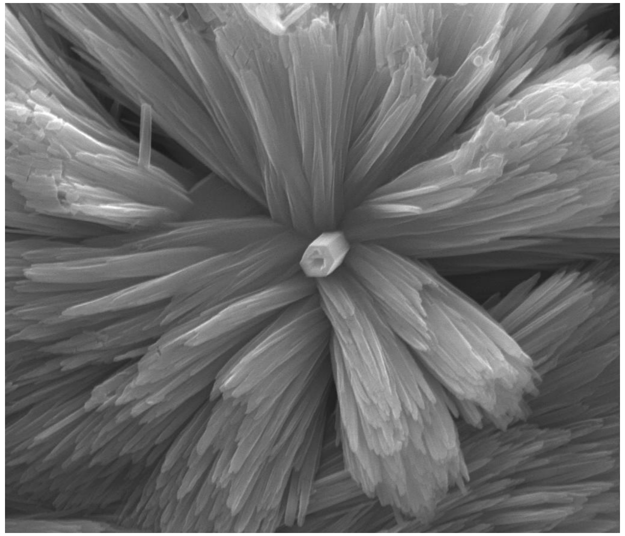
❖ Research goal (suggested)



ZnO nanomaterials for sensing

❖ZnO nanostructure for UV-sensing material

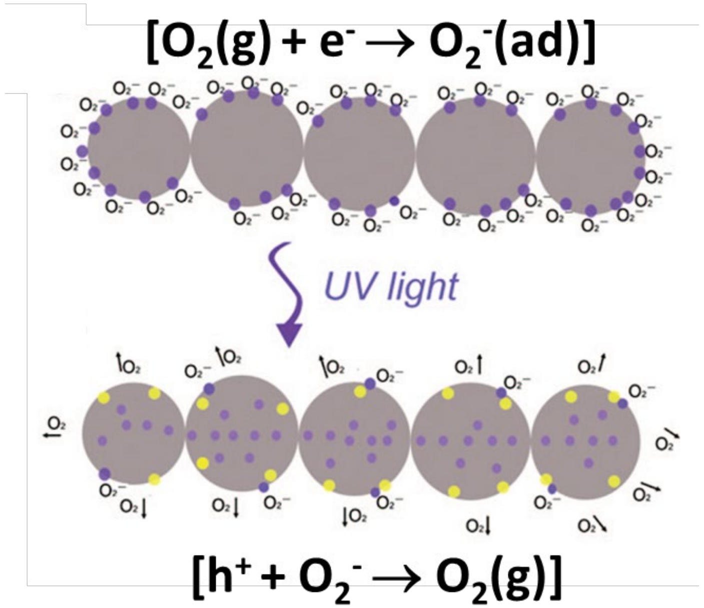


1. **An environmentally friendly semiconductor**
2. **Band gap of 3.35 eV**
3. **Various synthetic methods, diverse processing technologies**
4. **Operating at high temperatures and in harsh environments.**

Nanostructure ➡ Large surface area ➡ High sensitivity

ZnO nanomaterials for sensing

UV sensing mechanism of ZnO devices



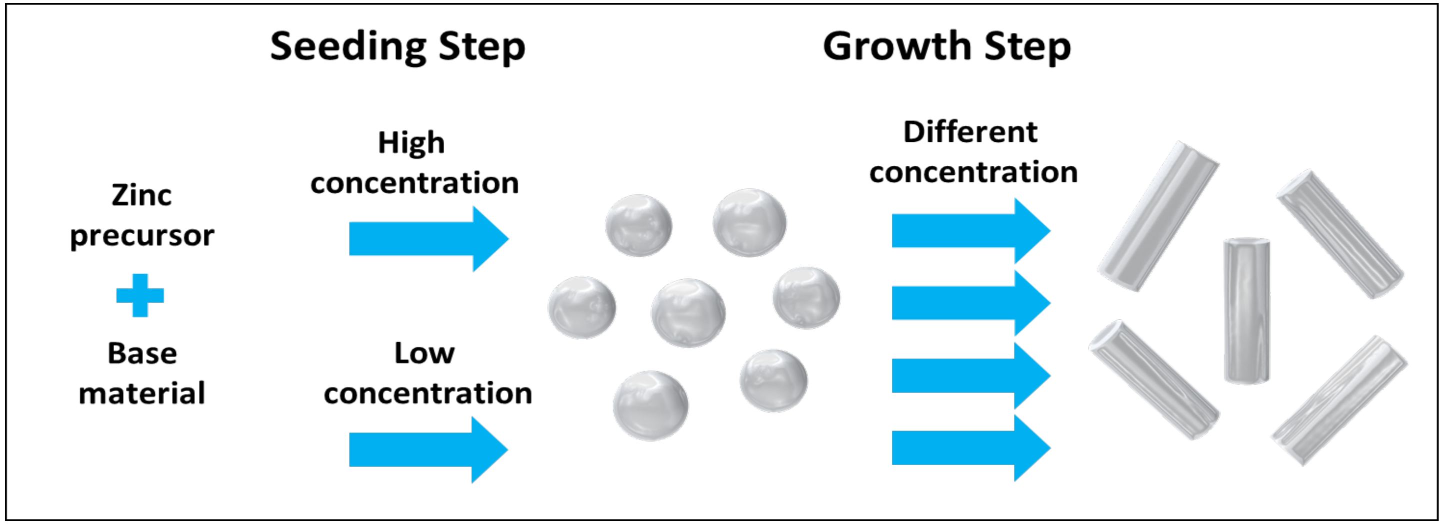
- Oxygen molecules are adsorbed onto ZnO surfaces by capturing free electrons which creates a low-conductivity depletion layer

- Upon UV illumination, hole discharge the negatively charged adsorbed oxygen ions to photodesorb oxygen from the surfaces or effectively get trapped at the ZnO surfaces, resulting in an increase in the free carrier concentration

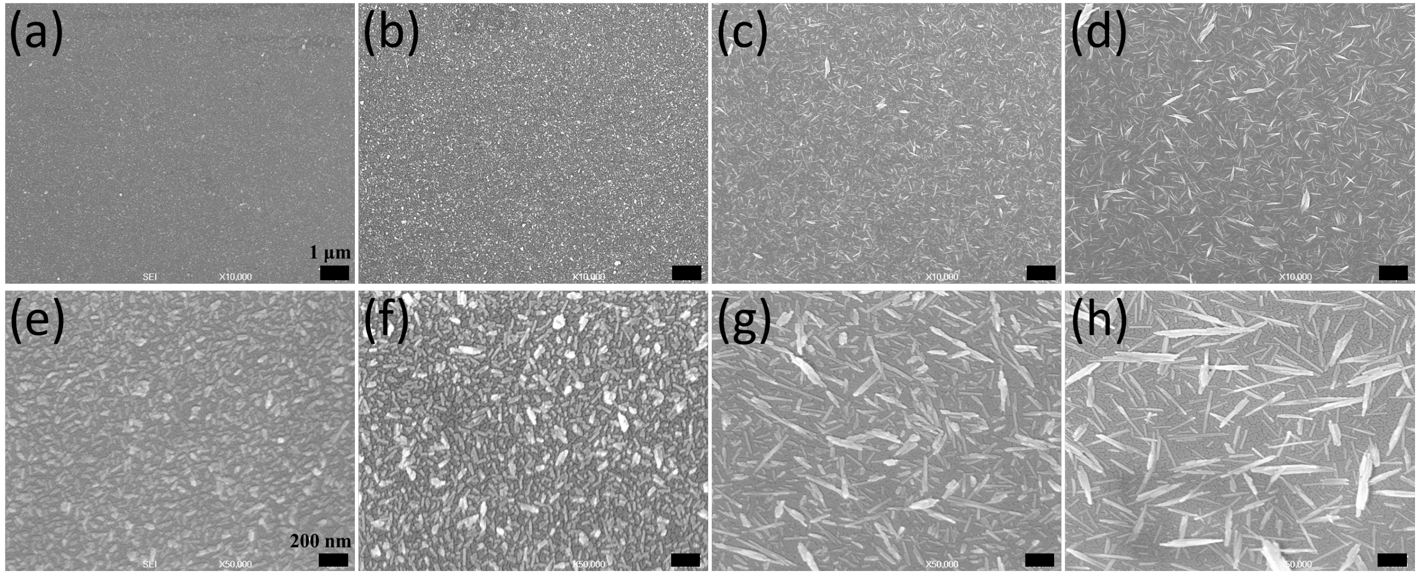
Objectives

To synthesize ZnO nanorods by solution-processing method with controlling the length of them to understand the affects of the length of ZnO nanorods on ZnO nanorods based UV sensors.

Research results

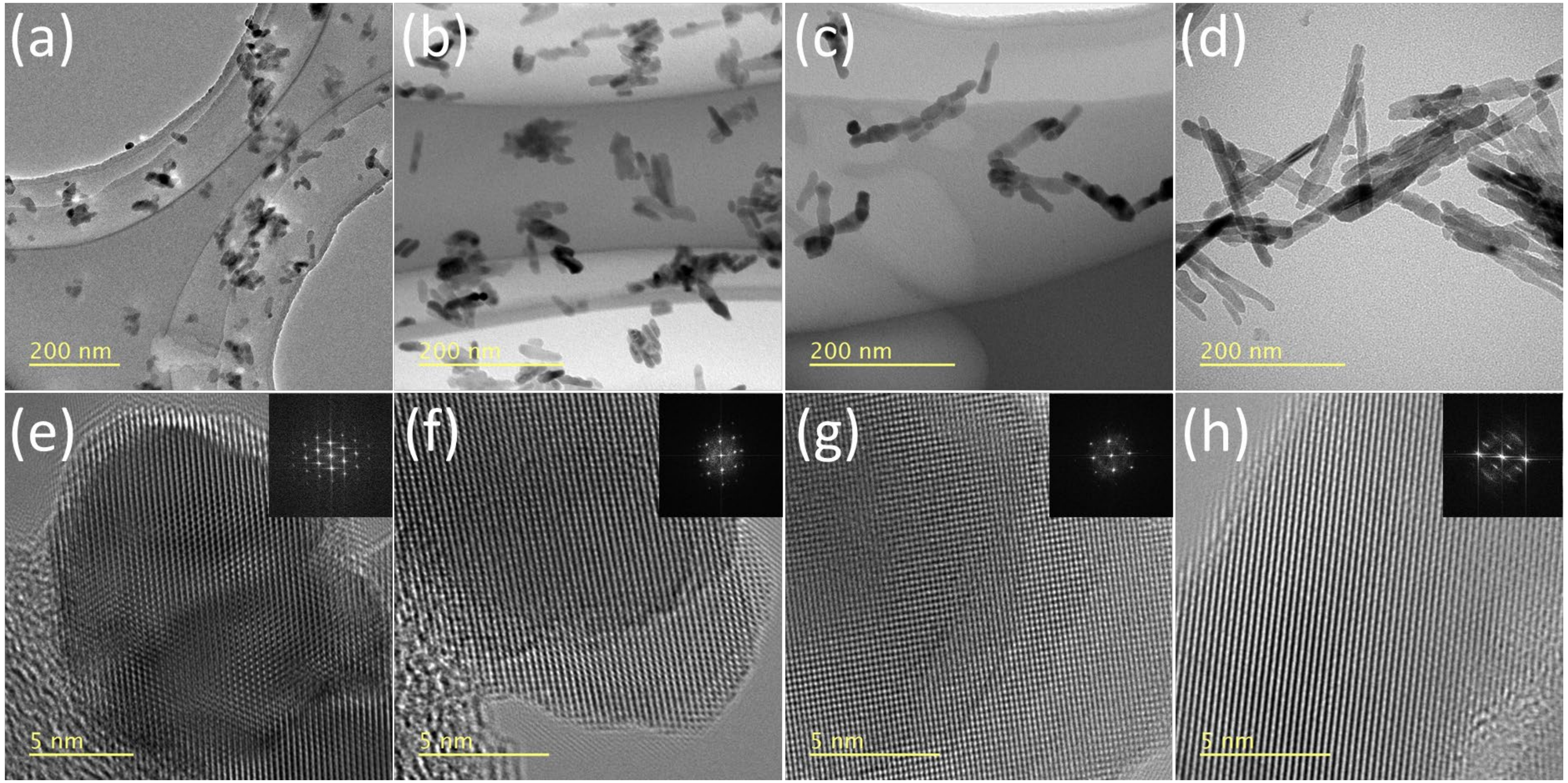


ZnO NRs synthesis by controlling the concentration of zinc precursors in the seeding and growth processes, respectively.



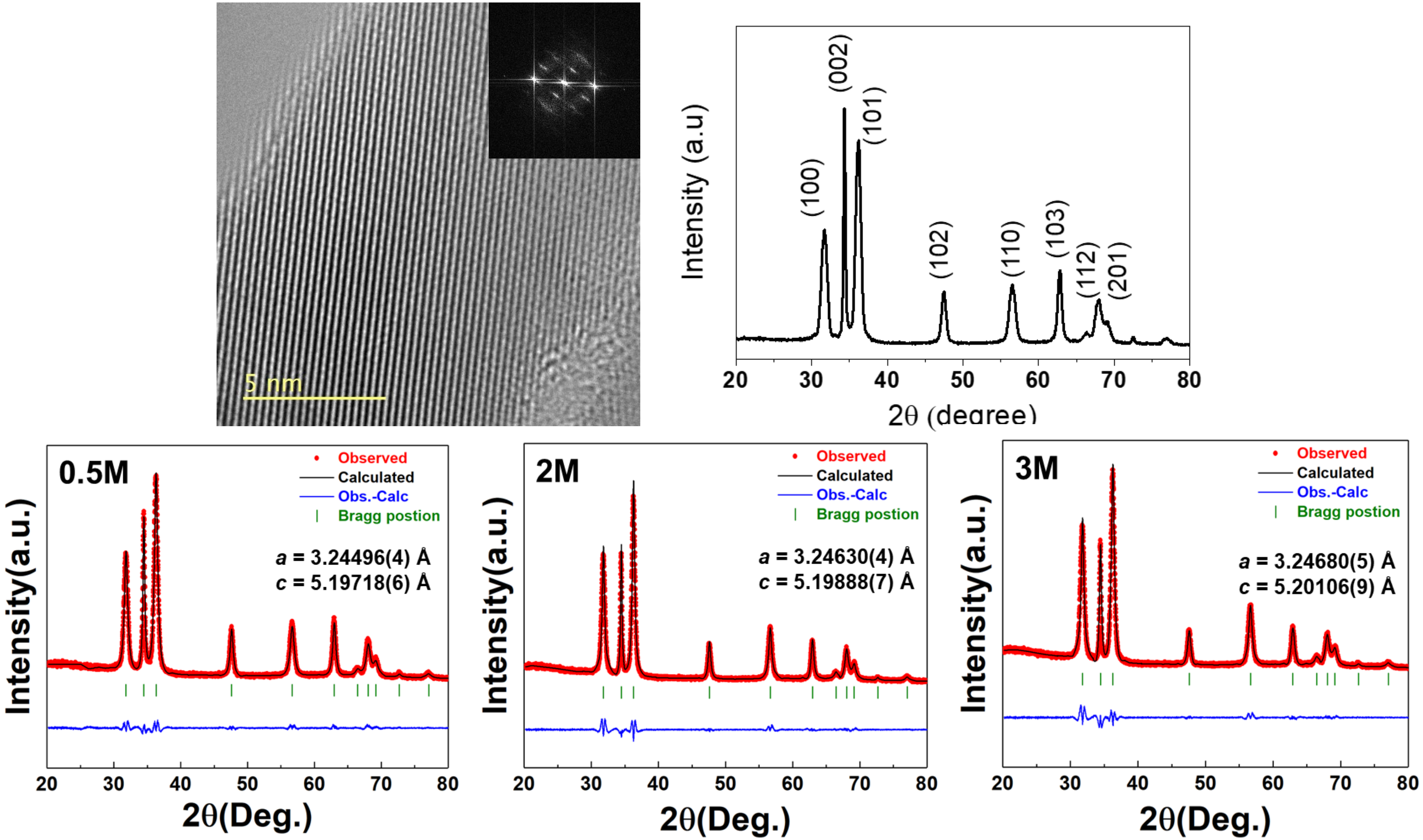
FE-SEM images of ZnO nanomaterials synthesized from different Zinc precursor concentrations of the growth reactions. (a) 0.5M, (b) 1M, (c) 2M, and (d) 3M concentration (Scale bar = 1 µm). Enlarged images (50,000x magnification) of the ZnO products (e) 0.5M, (f) 1M, (g) 2M, and (h) 3M respectively (Scale bar = 200 nm).

Research results



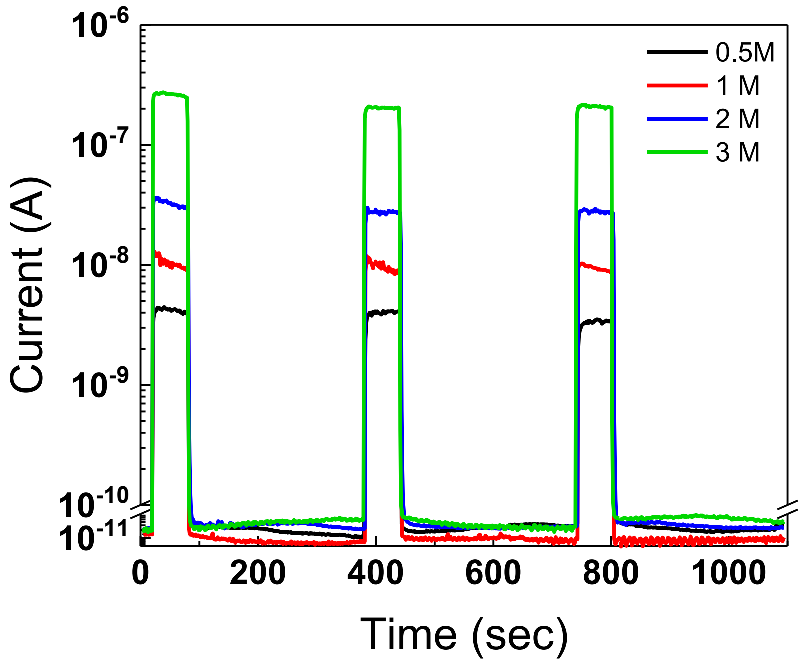
TEM images of ZnO nanomaterials with different aspect ratio synthesized from controlled precursor concentration such as (a) 0.5M, (b) 1M, (c) 2M, and (d) 3M. The crystal structure images and diffraction pattern of the product (e) 0.5M, (f) 1M, (g) 2M, and (h) 3M respectively.

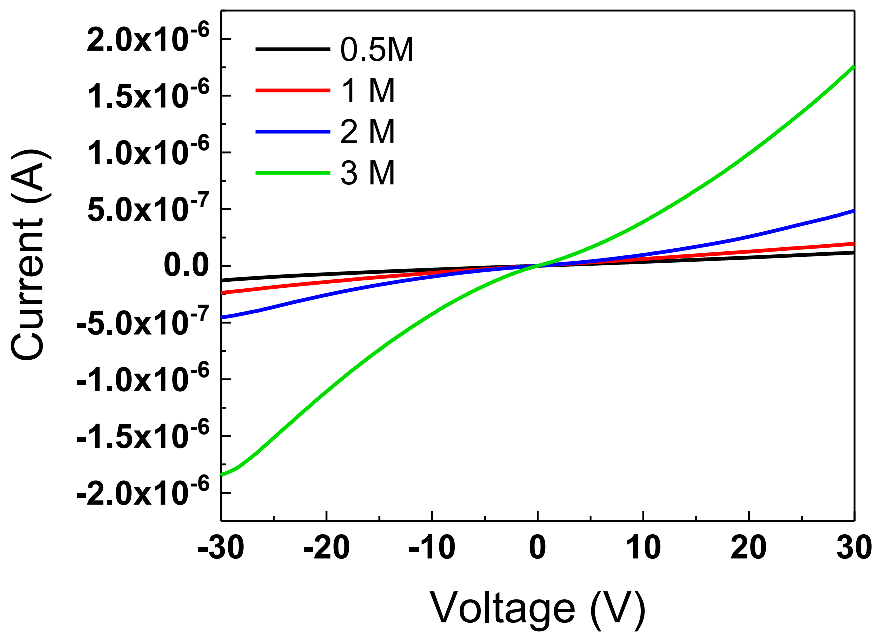
Research results



TEM and XRD pattern of ZnO nanomaterials with different aspect ratio

Research results





Growth reaction precursor concentration	Aspect ratio (average/maximum)	I_{UV} / I_{dark}	Response time (s)	Reset time (s)	Responsivity (A/W)
0.5 M	-	2.62×10^{2}	5.15	1.10	9.46×10^{-3}
1 M	4.5 / 5.5	1.08×10^{3}	2.61	1.61	2.75×10^{-2}
2 M	13.5 / 20.1	1.35×10^{3}	3.00	1.50	7.58×10^{-2}
3 M	18.6 / 27.3	1.09×10^{4}	3.10	1.25	5.55×10^{-1}

Optoelectric properties of ZnO NRs under repeated UV irradiation on and off

Research results

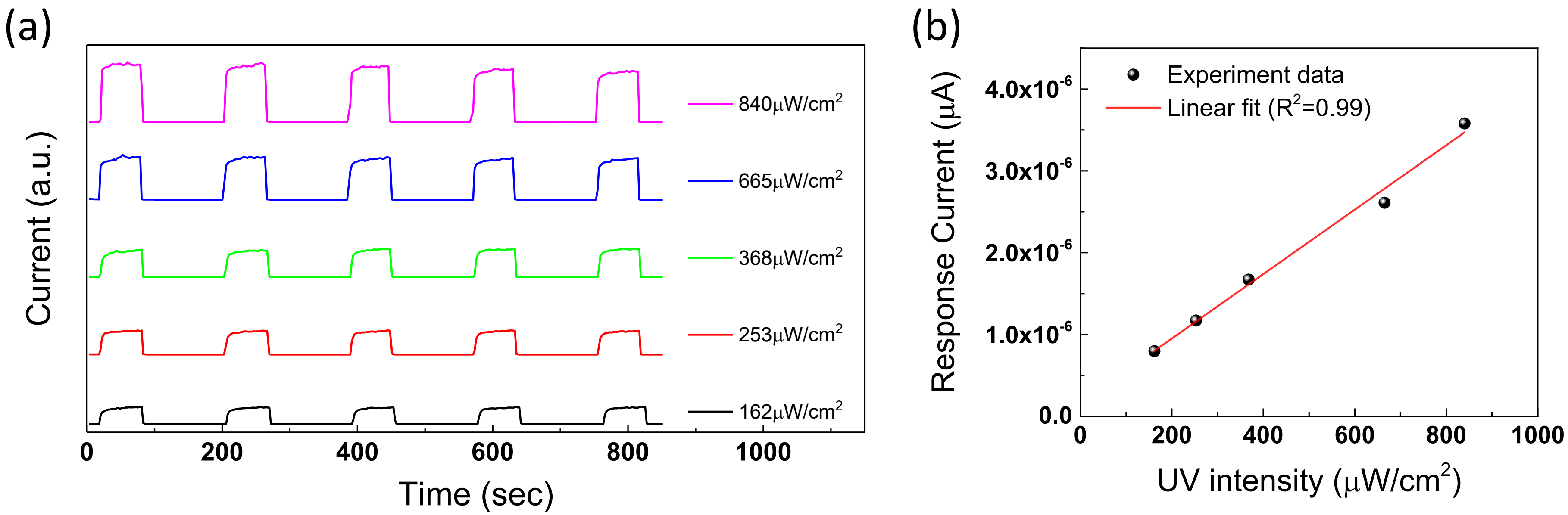
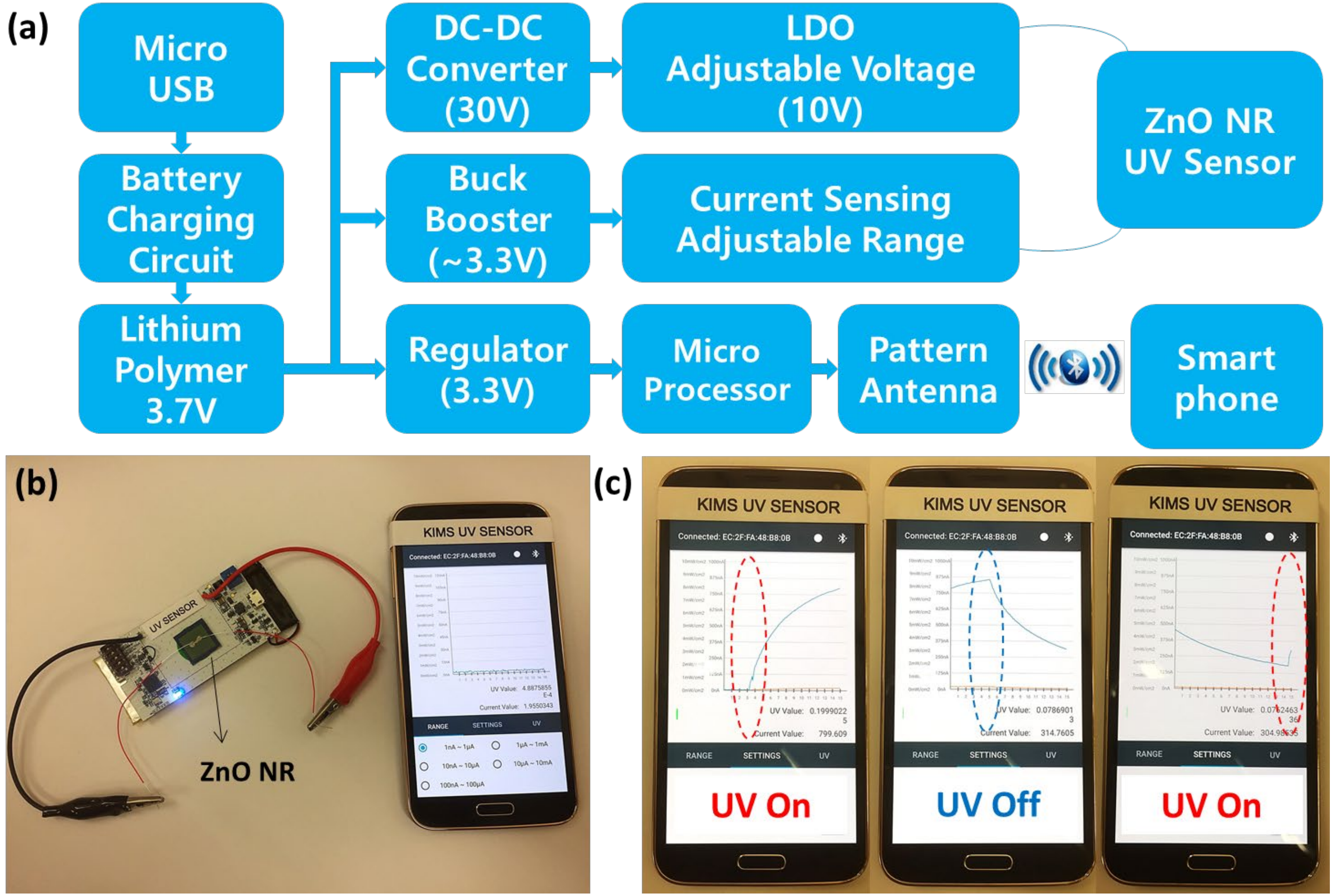


Figure. (a) Five times repeated photocurrent measurement under different UV intensity irradiation (162–840 μW/cm^2) (b) The photocurrent vs. UV intensity plot and linear fit for the calibration curve. (R^2 = 0.99)

Research results



(a) A schematic diagram of the circuitry for wireless ZnO NR UV sensor platform connected with a smartphone.

(b) A photographic image of the Bluetooth-connected ZnO NRs UV sensor module (left) and a smartphone display showing the dark current value in real time (right).

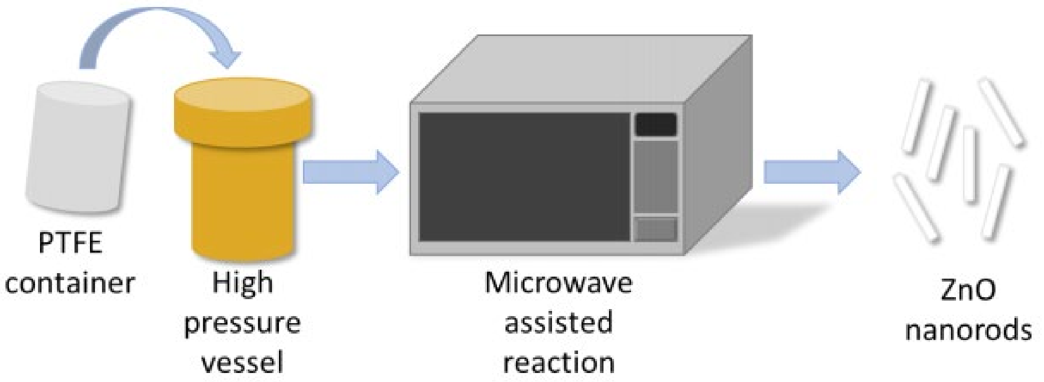
(c) Photographic images of the wireless ZnO NRs UV sensor operation under repeated UV light on/off.

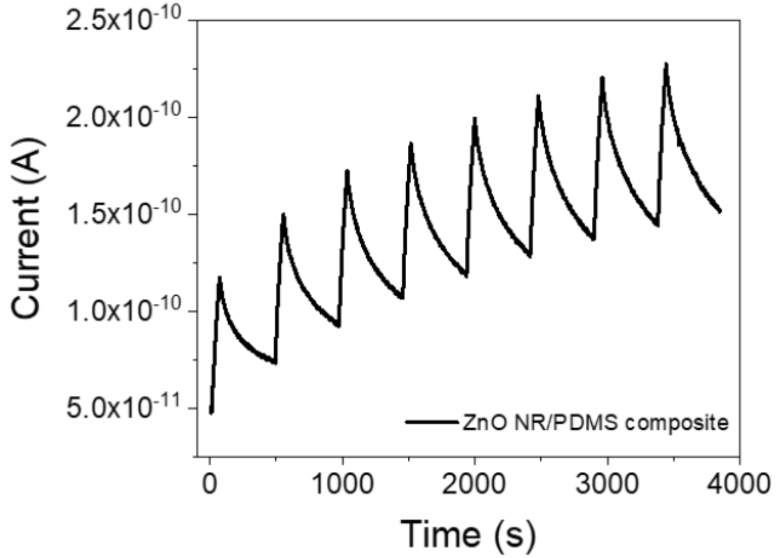
Research results

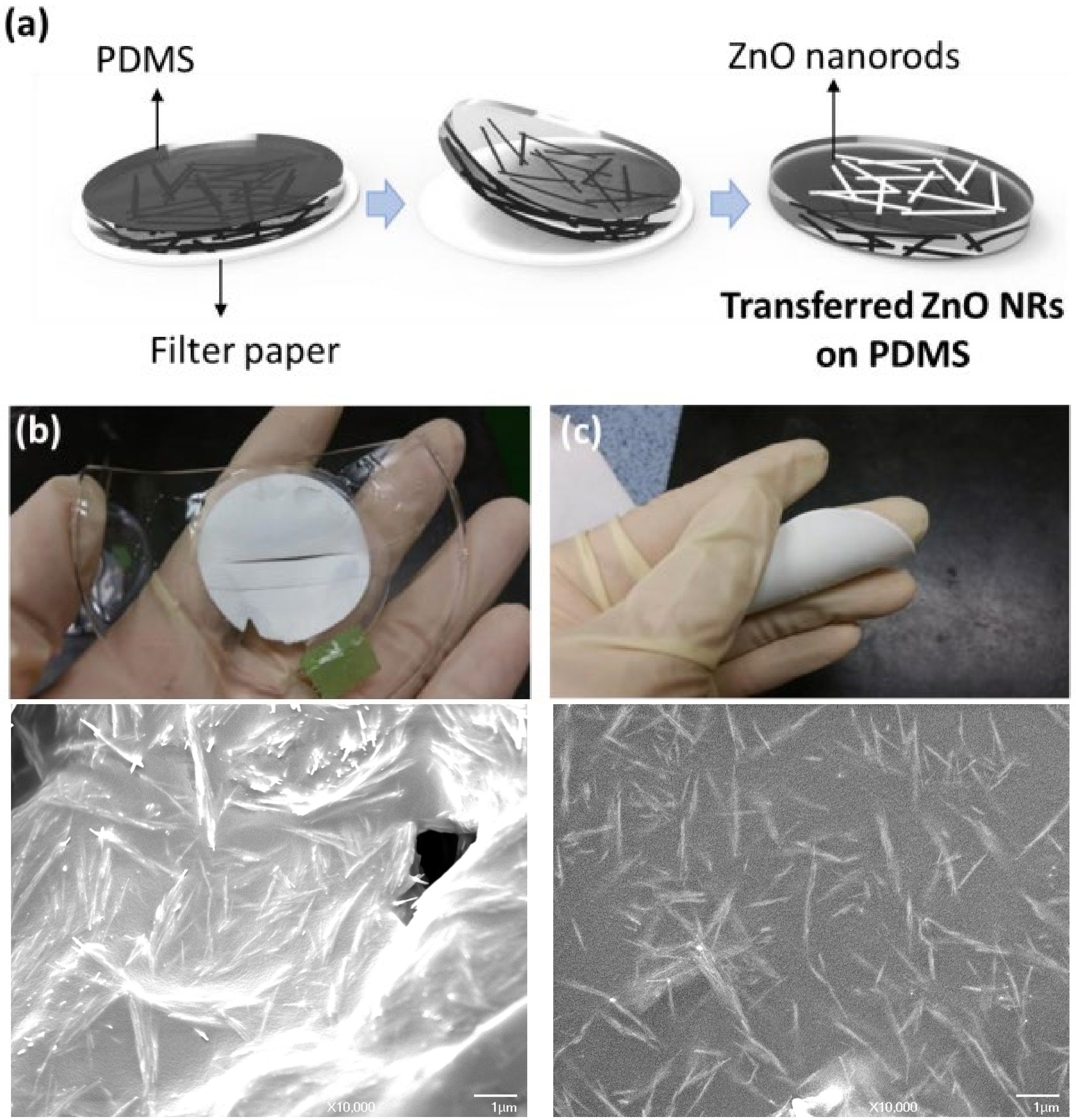
❖ How to make a flexible sensor? A fiber type?

Further research

- PDMS + ZnO nanorods Composite (1:1 weight ratio)

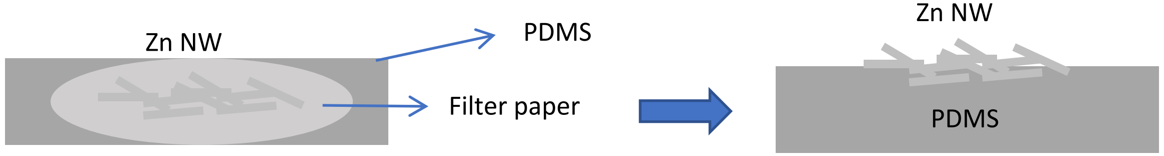


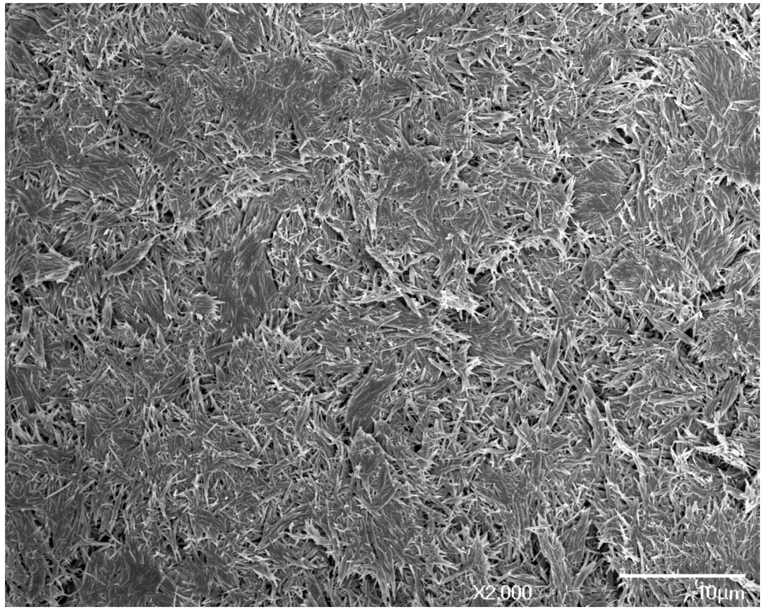


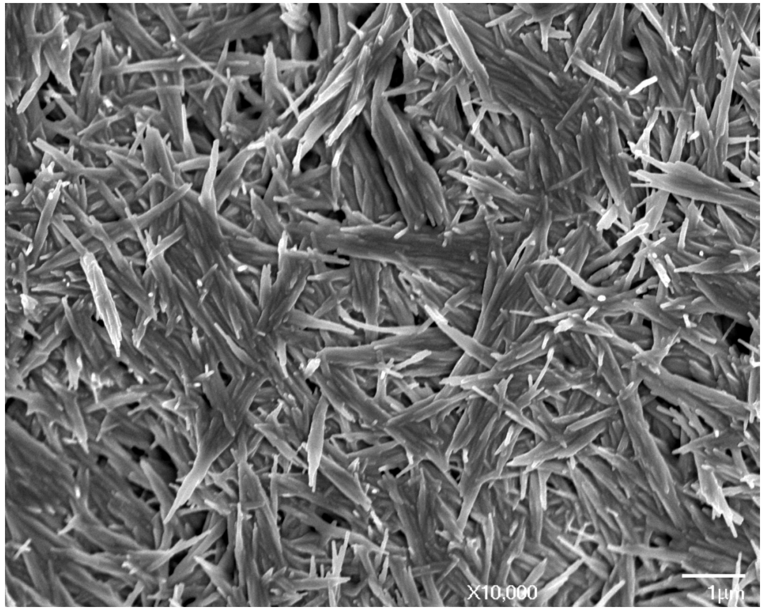


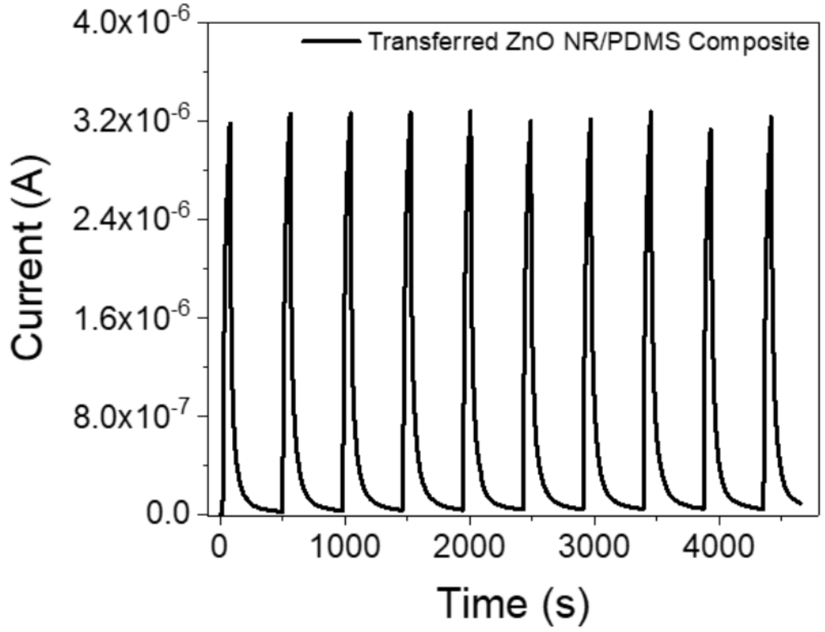
Research results

❖ **Transferred Composite (ZnO nanorods embedded PDMS)**







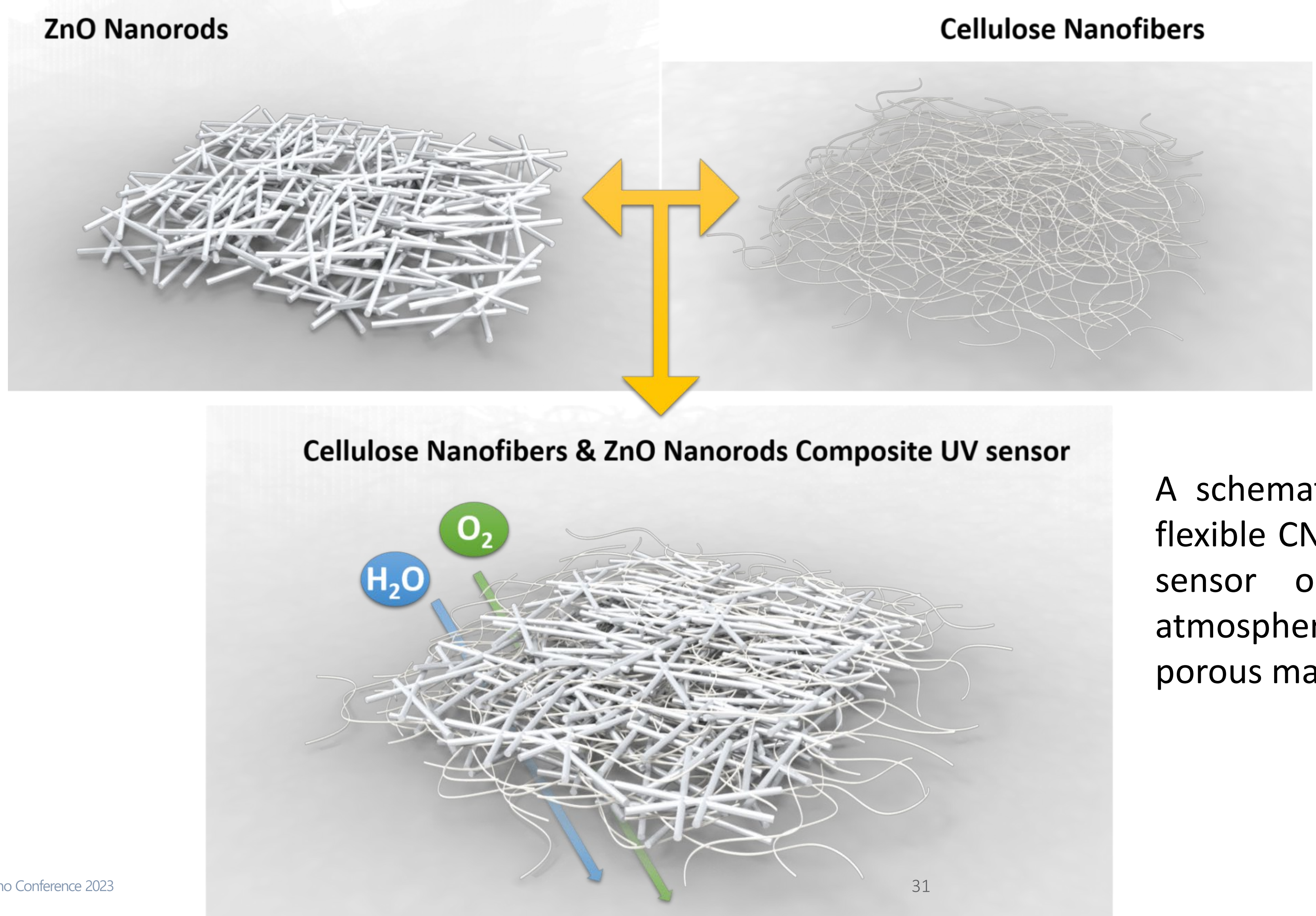


	Dark current	On current	On/off ratio
ZnO NRs/PDMS	-	-	1.84
Transferred ZnO NRs/PDMS	3.74×10^{-8}	3.26×10^{-6}	88.9

The optoelectronic properties of ZnO NRs/PDMS composite sensor

Research results

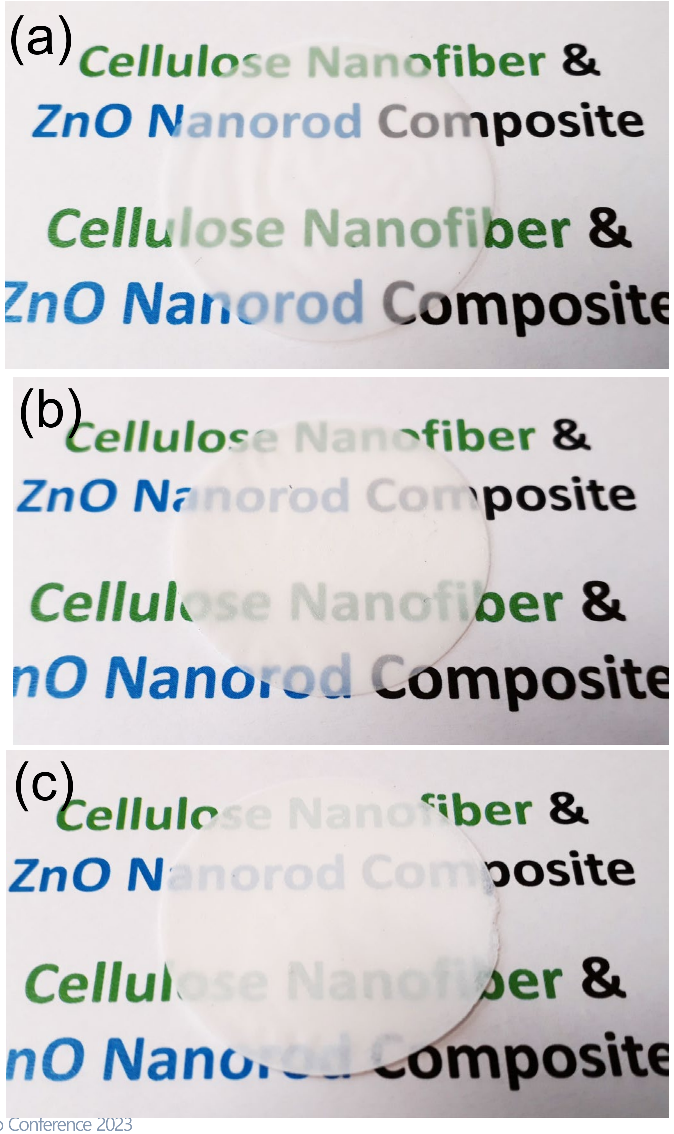
❖ZnO nanorods and CNF composite film for a flexible sensor

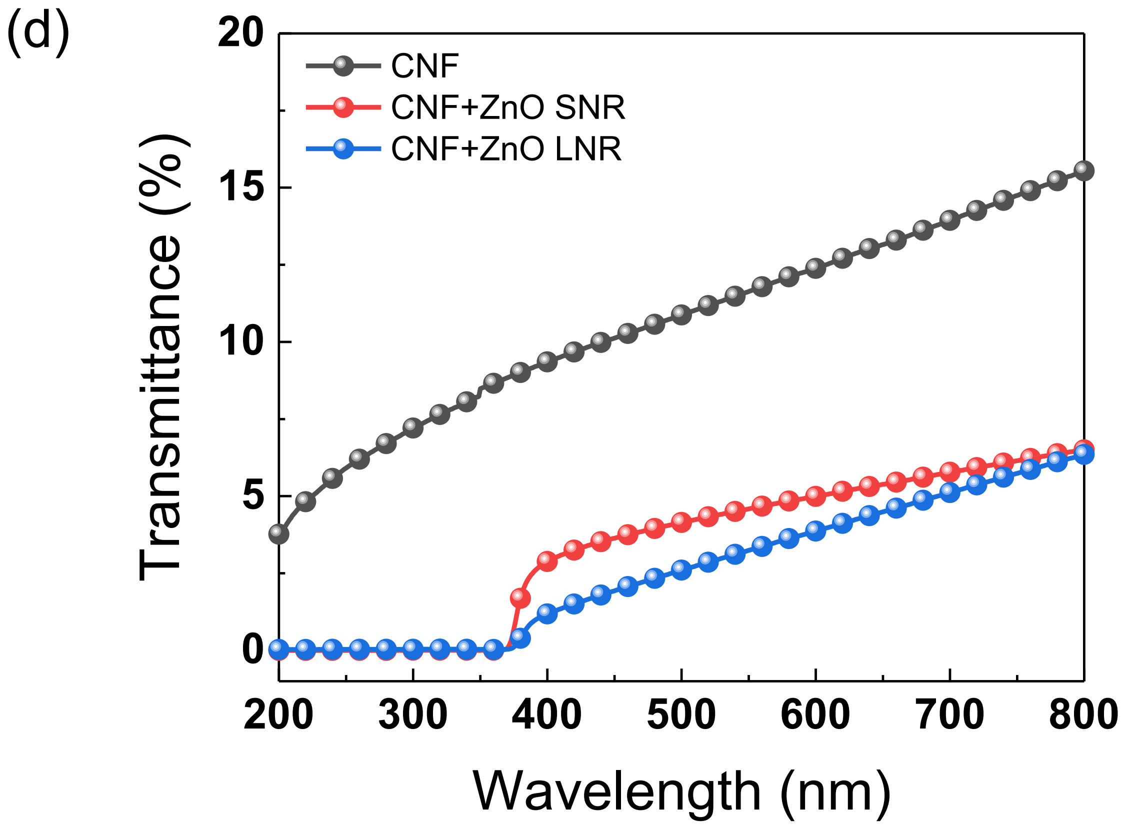


A schematic image of the fabrication of flexible CNF+ZnO NRs composite sheet UV sensor operating appropriately under atmospheric conditions based on the porous matrix materials.

Research results

❖Optical property of ZnO nanorods and CNF composite films

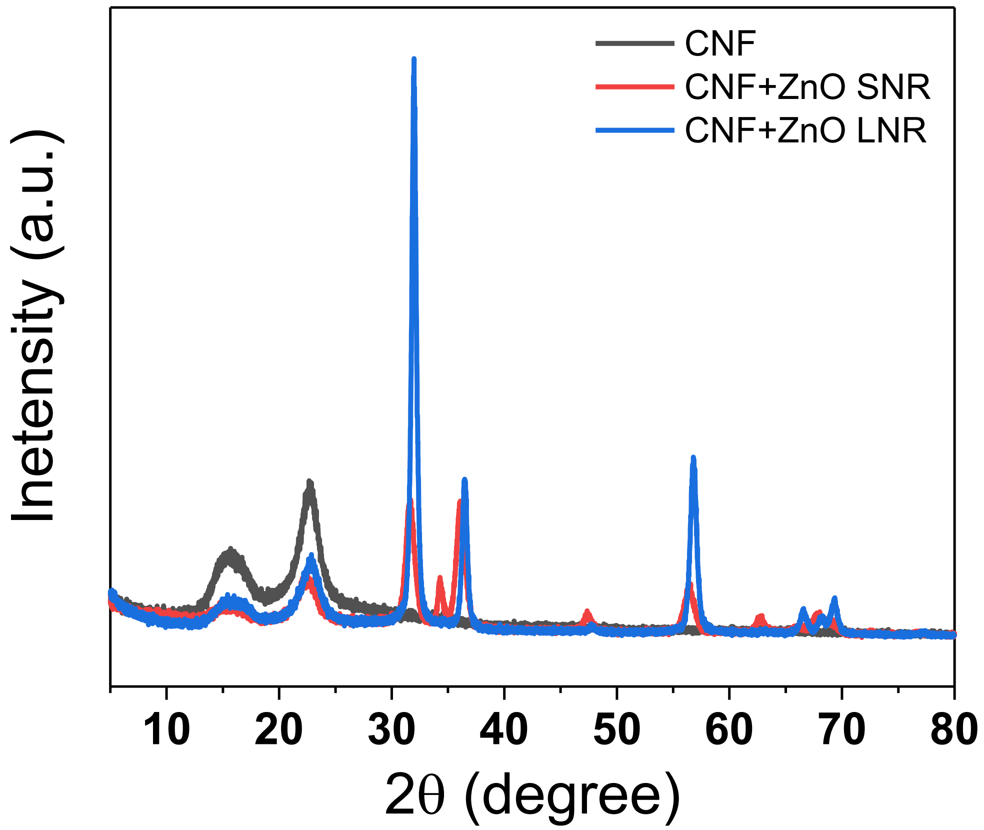




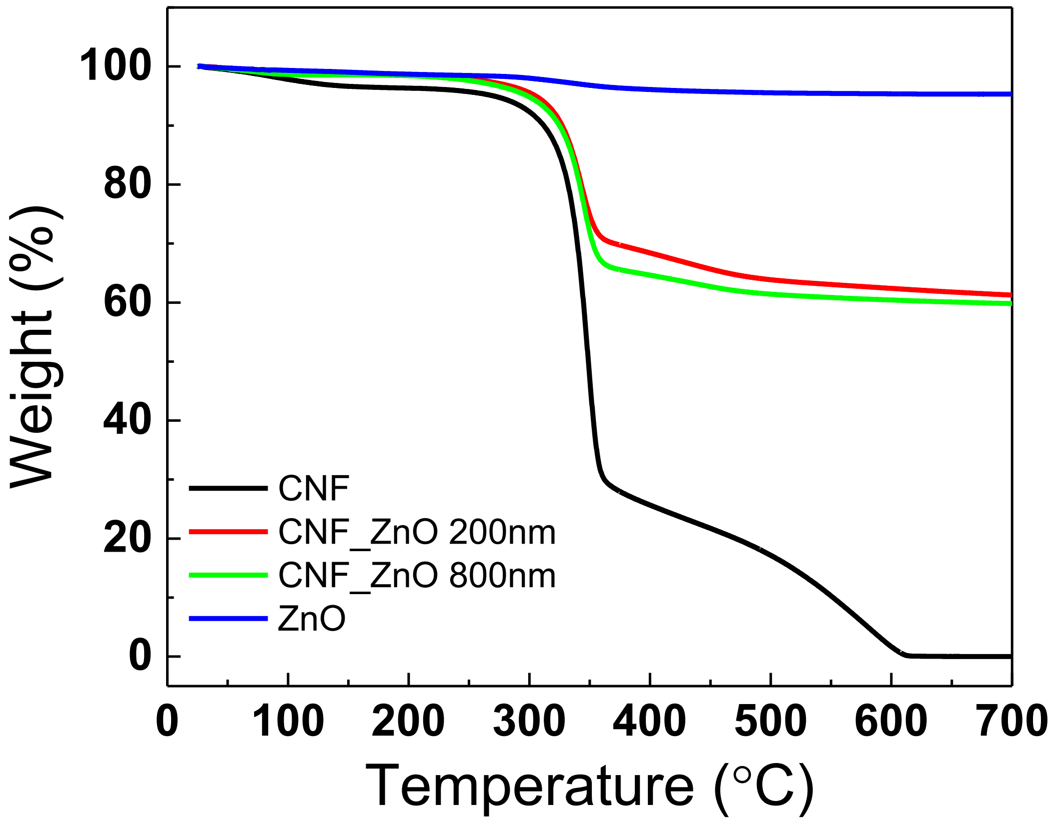
Photographic images of free-standing (a) CNF sheet, (b) CNF-ZnO SNR composite sheet, and (c) CNF-ZnO LNR composite sheet. (d) UV-Vis (Transmittance) spectra of CNF sheet and CNF+ZnO NR composite sheets.

Research results

❖ Crystal structure and thermal analysis of the composite sensor



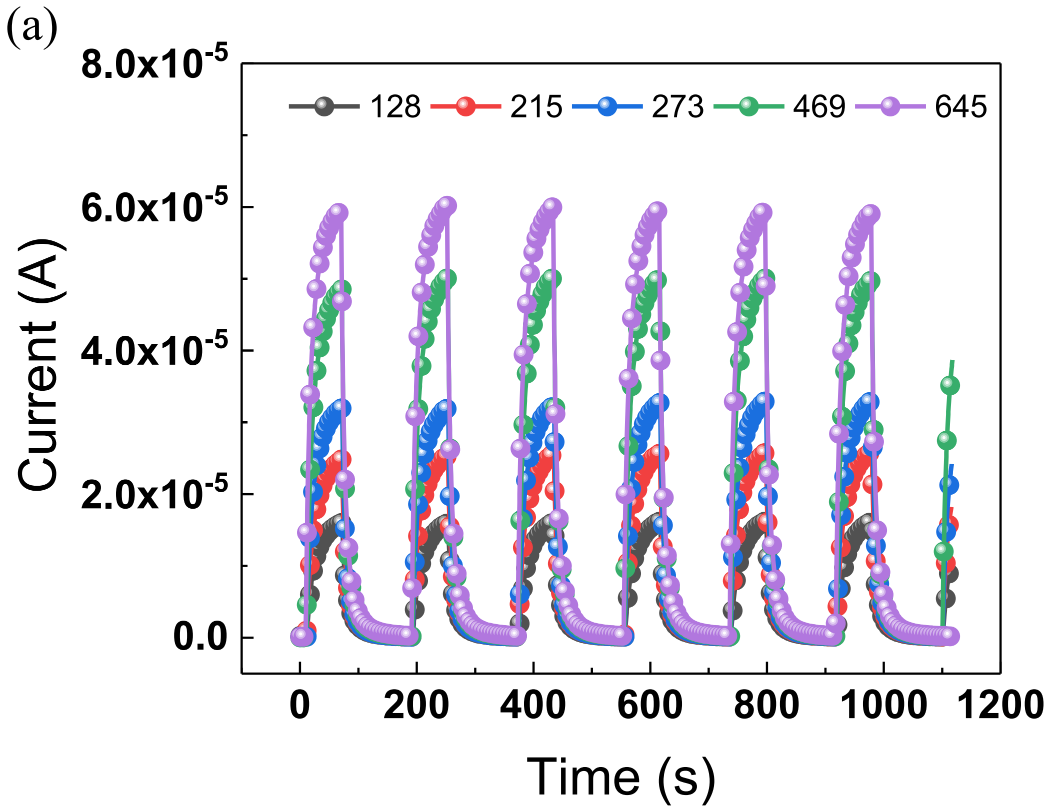
XRD pattern of CNF film and CNF-ZnO NR composite films with different lengths of ZnO NRs.

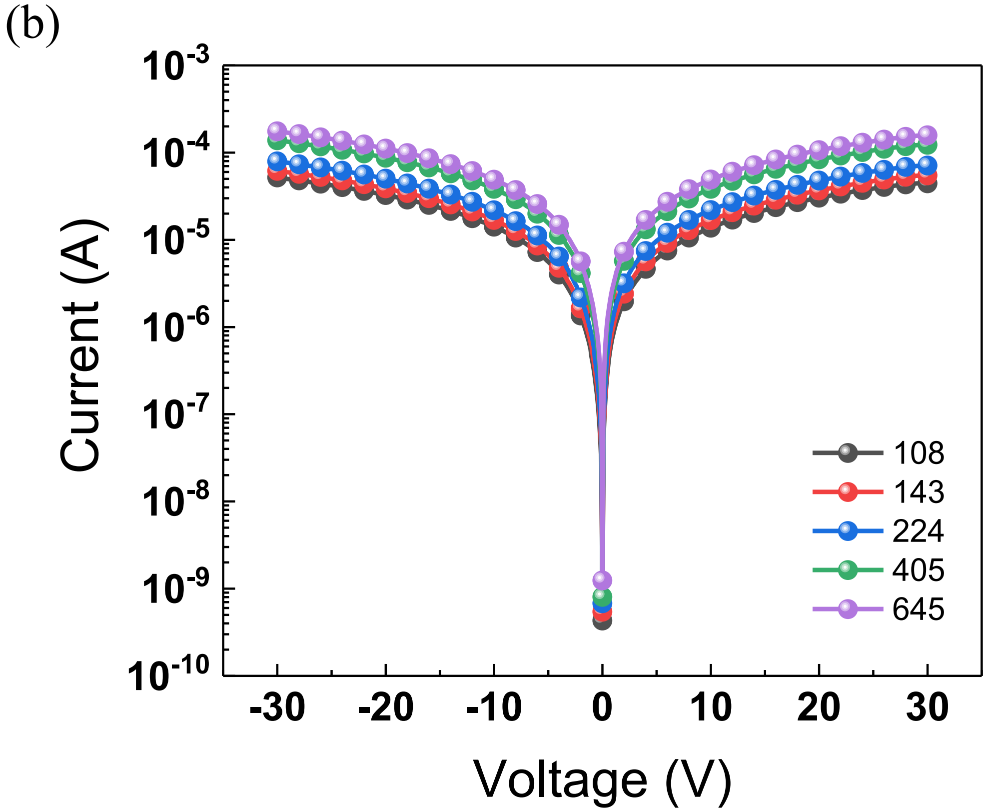


TGA spectra of CNF, ZnO, and composites

Research results

❖ Optoelectronic properties



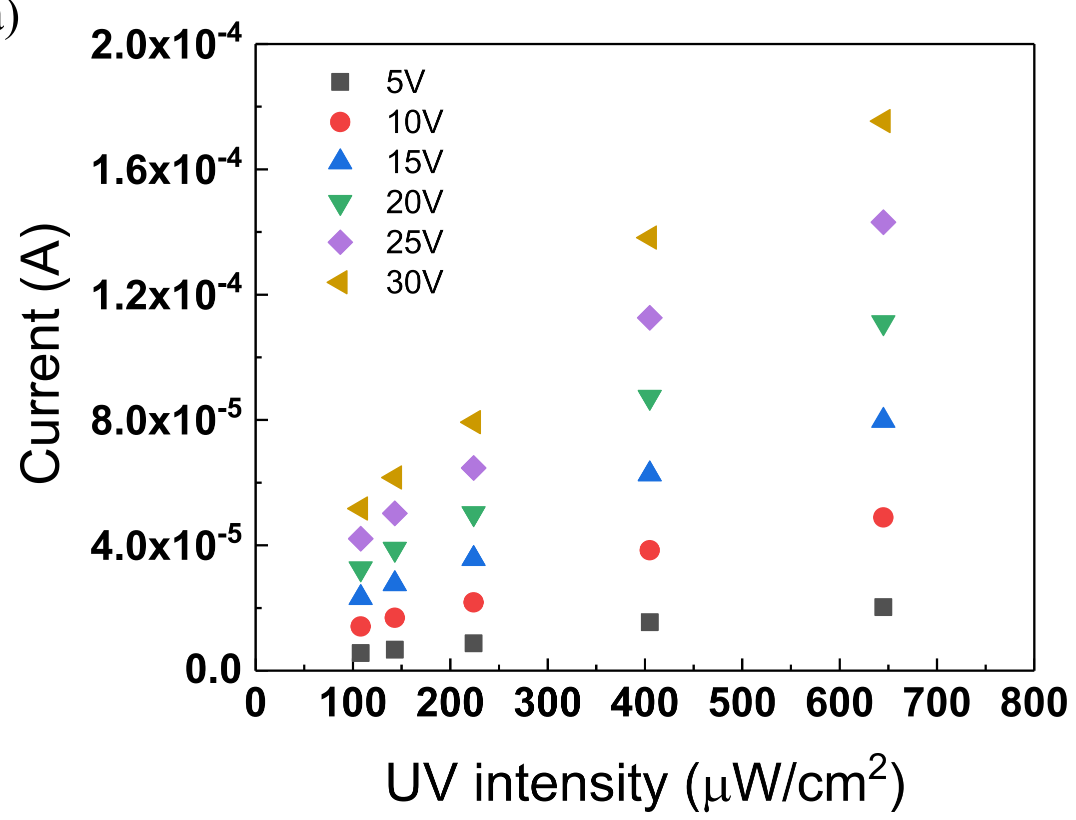


(a) Optoelectronic properties of ZnO NRs under repeated UV irradiation on and off (Intensity: from 128 to 645 μW/cm^2). (b) I-V curve of ZnO NR UV sensors.

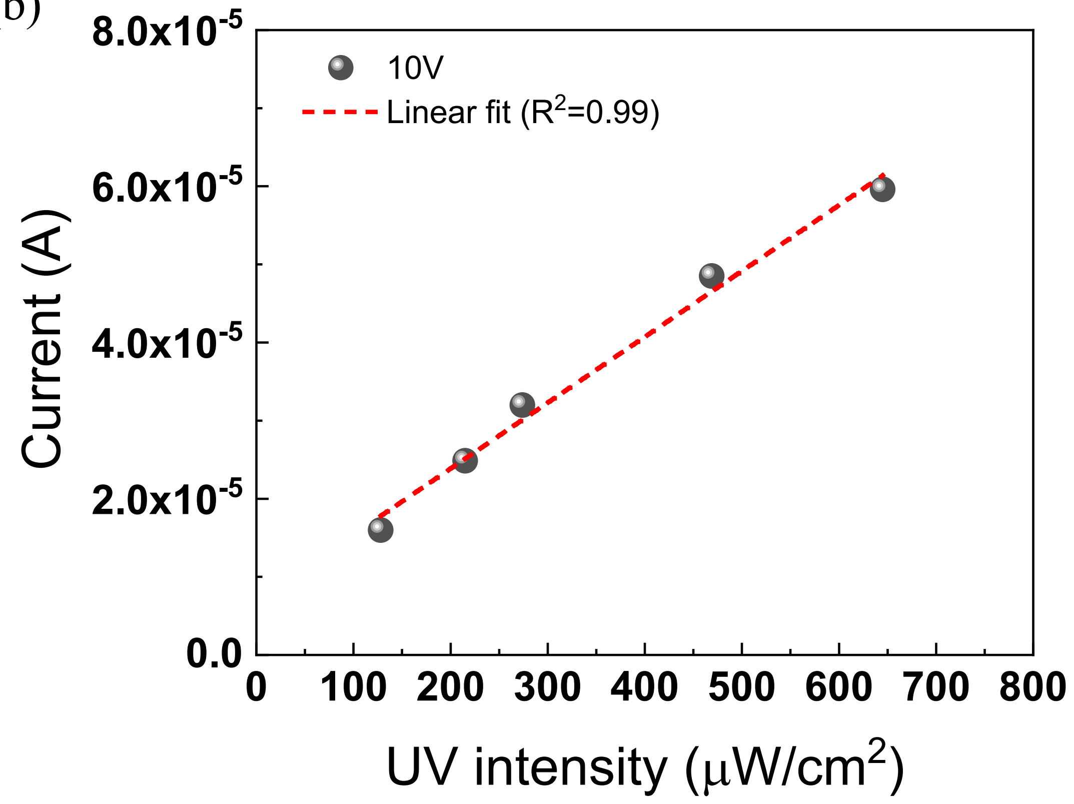
Research results

❖ Optoelectronic properties

(a)



(b)

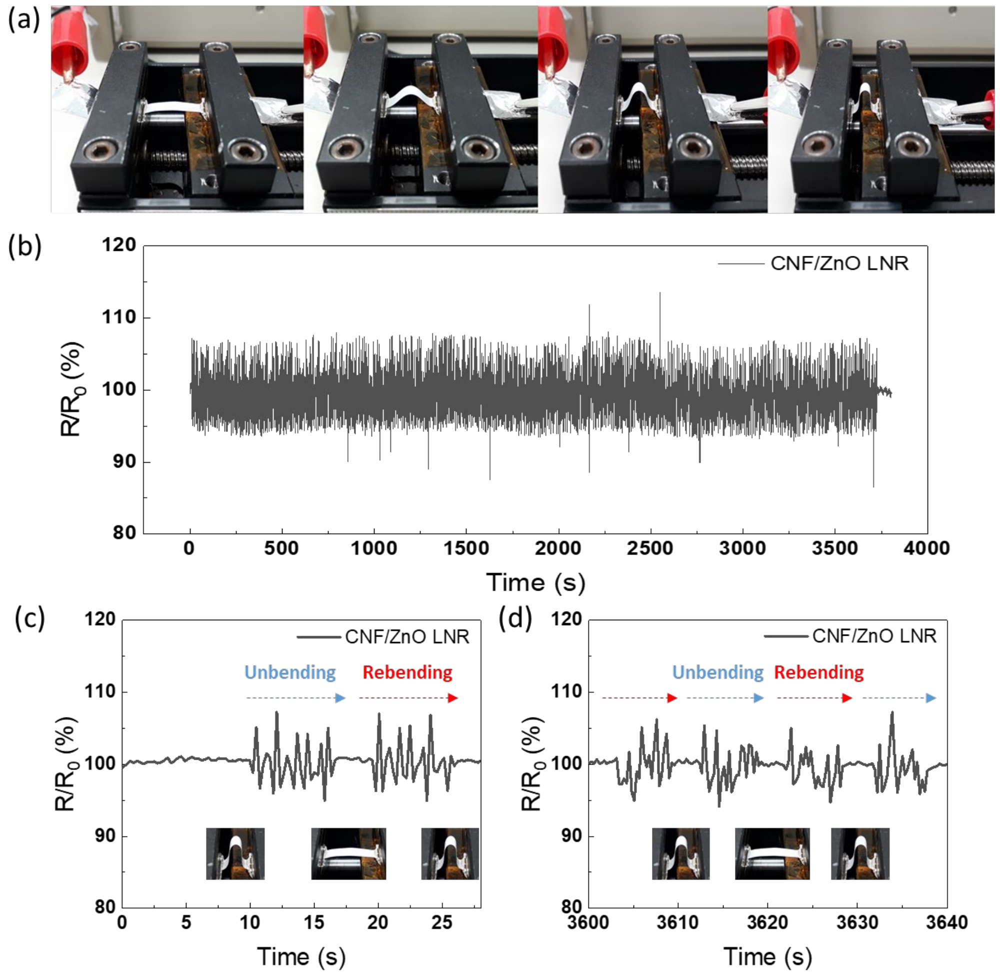


(a) Optoelectric properties of ZnO NRs under different UV irradiation and bias potential.

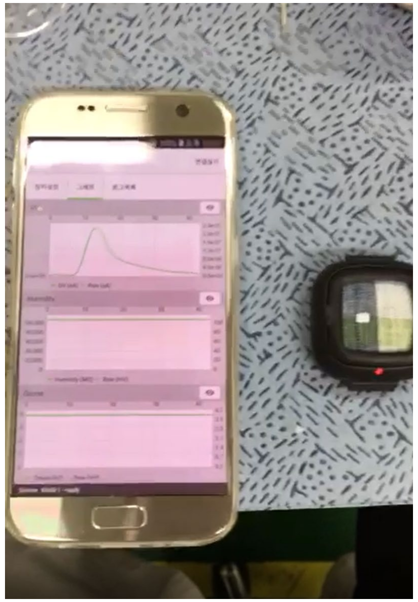
(b) The photocurrent vs. UV intensity plot and linear fit for the calibration curve. (R^2 = 0.99)

Research results

Verification of flexibility and implementation of the wireless platform



Photographic images of the bending test and resistance change plot



- Design and manufacture of wireless circuits
- Development of a prototype in the form of a smartwatch
- Development of a smartphone-linked wireless sensing platform

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04 Conclusion

Conclusion

- Cellulose nanofibers were fabricated by delicate nano fibrillization.
- The rheology properties were suggested to estimate the degree of nano fibrillization.
- Aspect ratio controlled ZnO nanorods were successfully synthesized via two-step processes.
- As the length of ZnO nanorods was longer, UV responsivity was 58.5 times higher.
- Flexible sensors with high sensitivity based on inorganic and organic 1-dimensional nanomaterials.
- Cellulose nanofibers can make a porous nano matrix for inorganic sensing materials.
- Composites sensor was successfully prepared for wearable devices.

Acknowledgement

KIMS MEMBERS

Dr. Ajeong Lee
Sangjun Hong
Sanghyeon Ju
Youngeun Shin

RESEARCH FIELDS

Conductive polymer synthesis and their applications
Flexible energy harvester
Organic photo-electric materials

CNT & Graphene composites
Carbon fiber composites
Fiber-based energy storage, sensor
Sustainable polymer composite
Cellulose-based nano-composite (Insulation, SAP)


Thank you!