KOREA UNIVERSITY

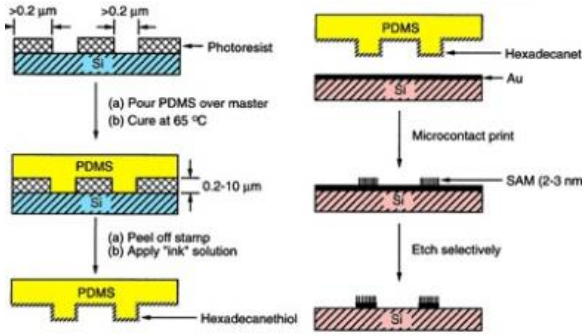
Biomimetic Hierarchical Structures for Low Power Gas Detection

Byung Yang Lee
Mechanical Engineering, Korea University

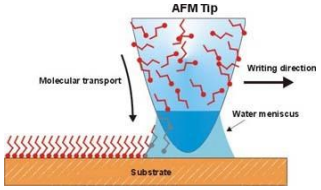
Jul 12, 2018

Contents

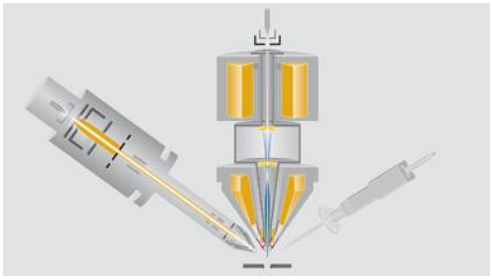
Man-made Hierarchical Structures



Soft Lithography

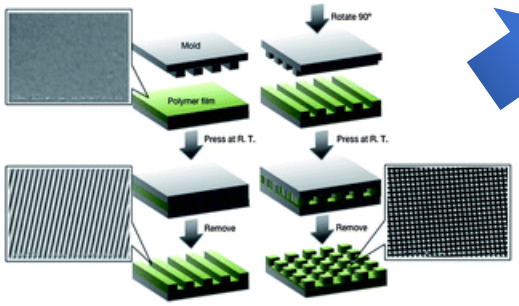


Dip-pen Nanolithography

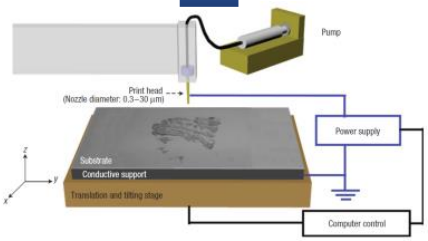


FIB Lithography

Complex Structures



Nanoimprint Lithography



Jet-printing Lithography

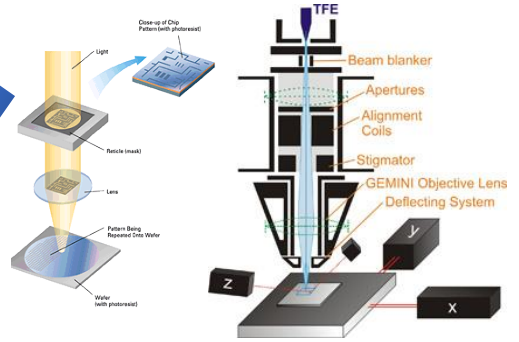
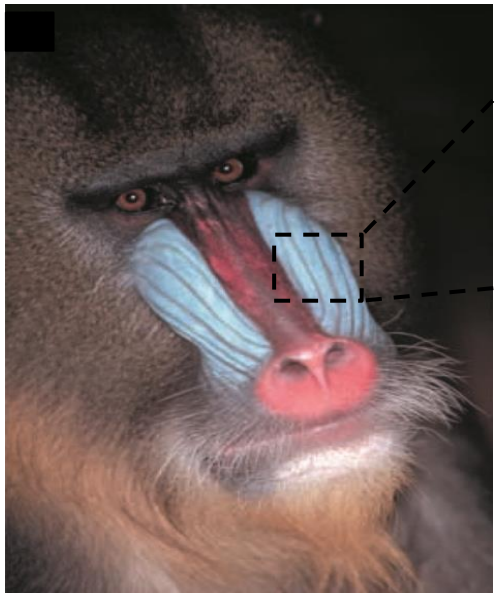
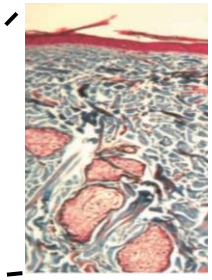
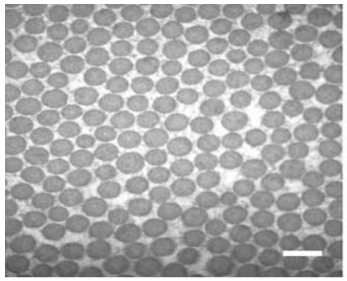


Photo & E-beam Lithography

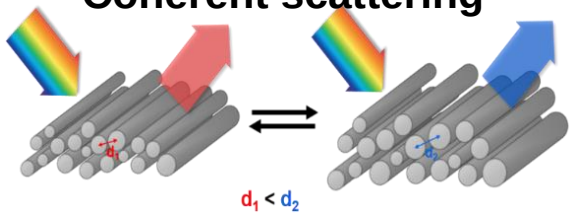
Colors in Nature





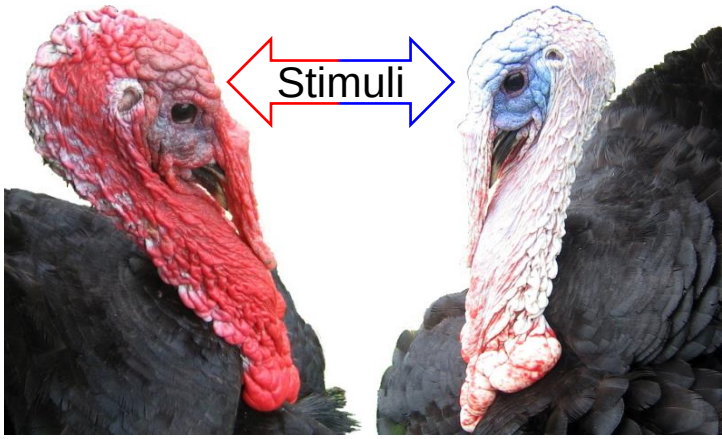


Coherent scattering



$$2nd sin\theta = m\lambda$$

Seven-faced Bird (七面鳥)



In nature, **structural color** can be achieved through the interference effect of ordered fibrous nanostructures which scatter light coherently

Turkey can change their skin color by expansion of the collagen structures.

Oh et al, Nature Communications, 2013

One Example: Cellulose

- Structural color in plants

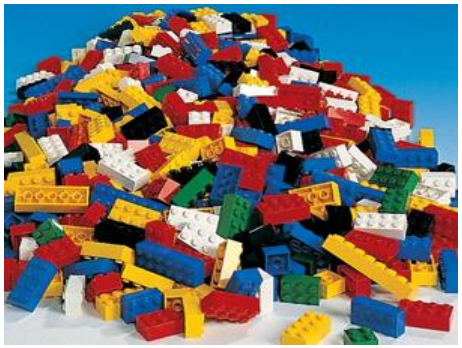
  Circularly polarized reflectance of cellulose film

- Structural color of leaf beatles

  Vivid color of Cellulose nanocrystals self-assembly

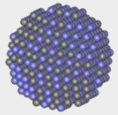
Vignolini, Silvia, et al. "Pointillist structural color in Pollia fruit." Proceedings of the National Academy of Sciences 109, 15712 (2012).

Let's Learn from Nature



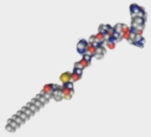
Assembly of Nano & biomaterials

Nano & Biomaterials (Basic Building Blocks)

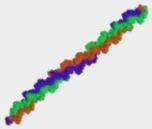

NPs


Chitosan


Cellulose


Proteins


Virus


Peptide

New Function Devices (Complex Building)

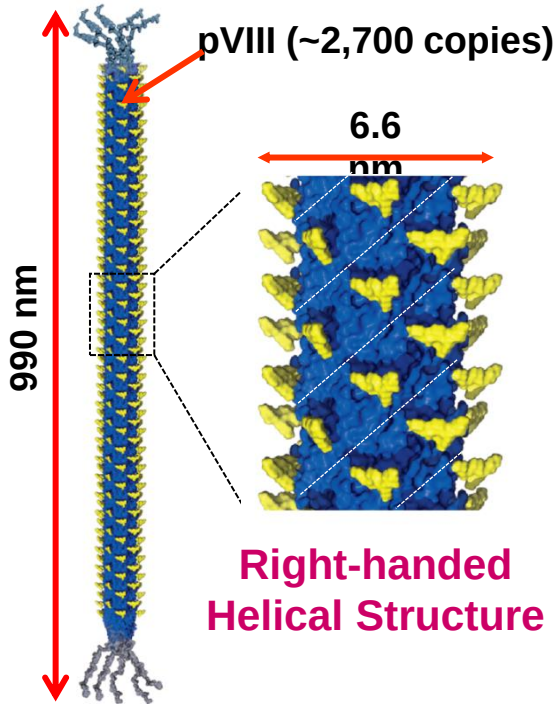

High-power Energy Devices
(Piezoelectric Devices, Solar Cells)


High-efficiency Electric Devices
(Photodetectors, FETs, FEDs)


Highly Sensitive Sensors

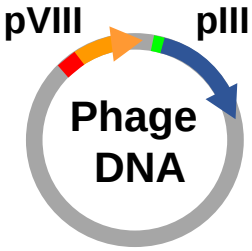
M13 Bacteriophage (Virus)

- **Structure of M13 Phages (Monodispersity)**



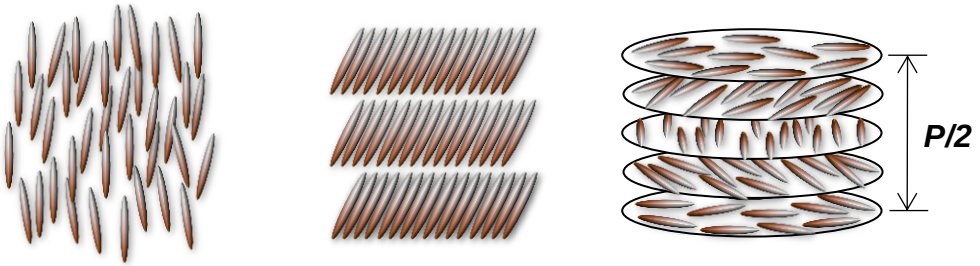
: Genetically incorporated functional peptide

- **Surface Modification via Genetic Engineering**



- 1E, 2E, 3E, 4E Phages

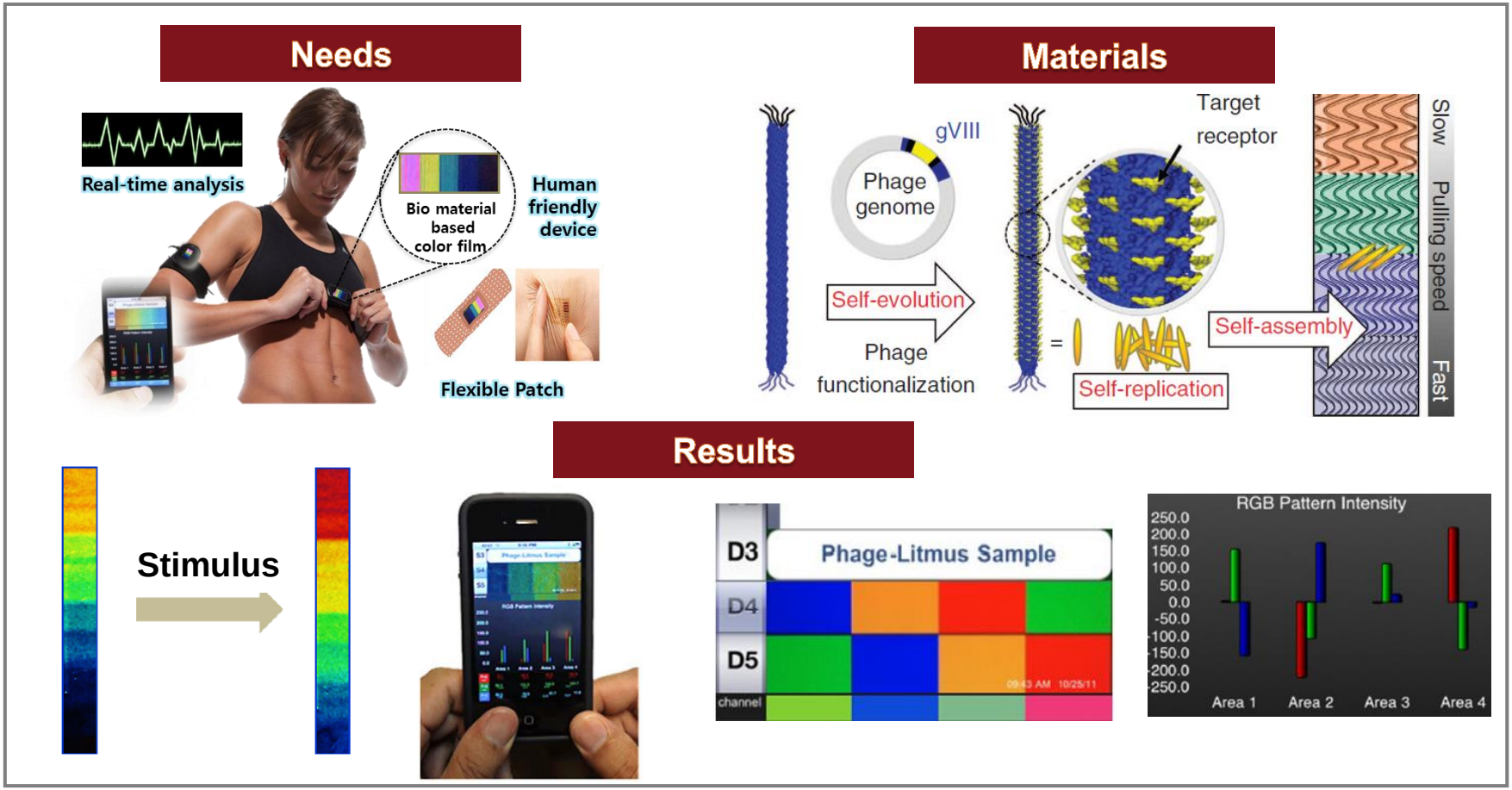
- **Liquid Crystalline Behavior**



Nematic Smectic Cholesteric

Virus-based Colorimetric Sensor

- **Measuring environmental hormones; Early Detection of Food Deterioration; Disease Diagnosis**
- **Material: Self-assembled virus film (M13 bacteriophage)**
- **Mechanism: Swelling/Deswelling of Phage Film → Color Change of the Film**



Oh et al, Nature Communications, 2013

Part Ⅰ. Cellulose nanocrystal (CNC films)

- Previous research
- Research concept
- Results

Research motivation : Nanocellulose

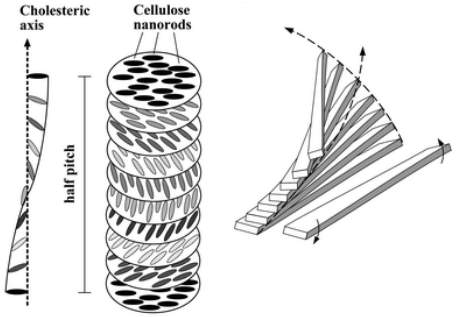
Cellulose in Nature

Low price

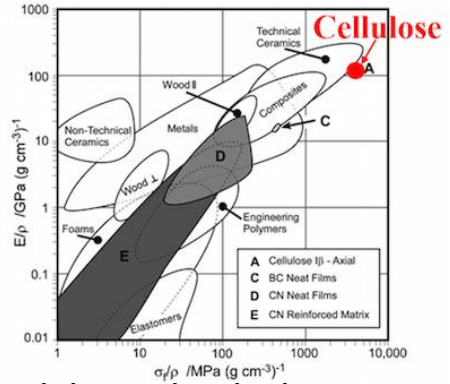
Bio-friendly

Bio-degradable

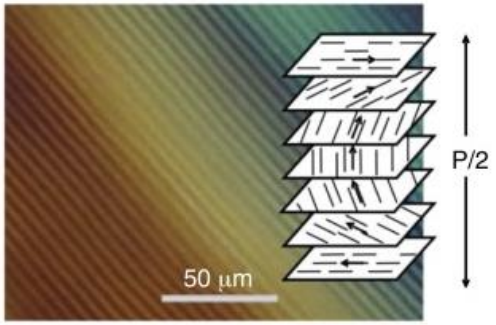
Cellulose in nanoscale



Self-assembly



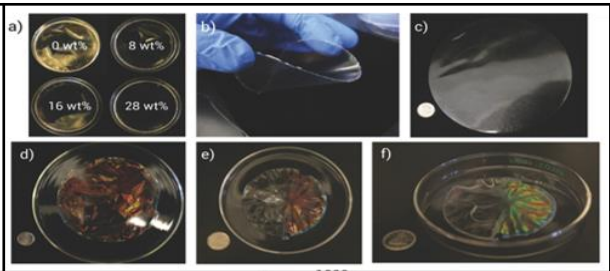
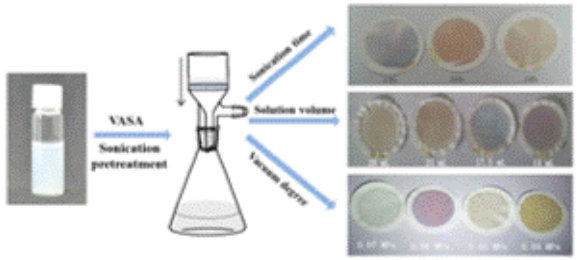
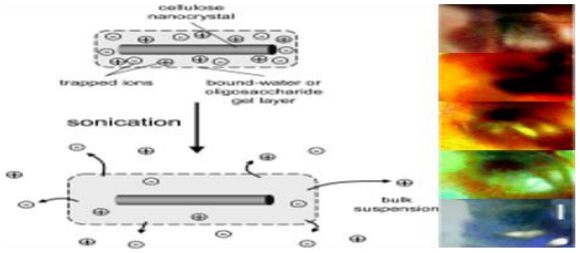
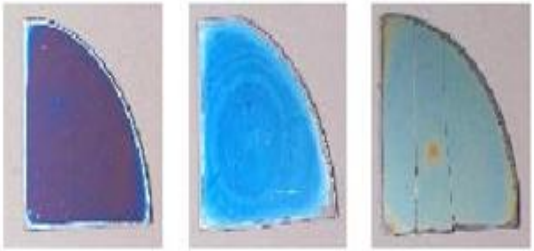
High mechanical property



Optical property

Crystalline Nanocellulose Films

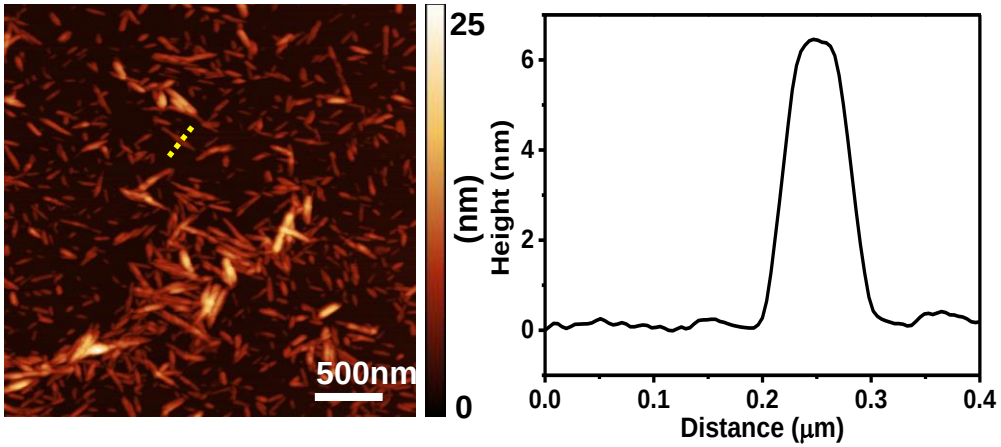
Previously four major techniques has been proposed…

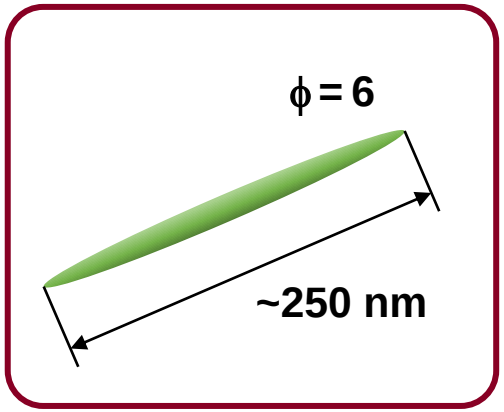
1. Chemical-additives		• Add chemical additives **to control the intervals of CNCs** • Ionic liquid, PEG, Glycerin, etc…
2. Vacuum-assisted		• Add chemical additives **to control the intervals of CNCs** • Fastest fabrication method • Limited substrate
3. Sonication-induced		• Add vibration energy **to control the intervals of CNCs** • Reversible process, hard to maintain
4. Spin-coated		• Mechanically laminated thin film • Limited thickness

Kelly et al. Advanced Optical Materials 1, 295 (2013); Chen, Qi, et al. Biomacromolecules 15, 4343 (2014); Beck, S. et al.. Biomacromolecules, 12, 167 (2010).

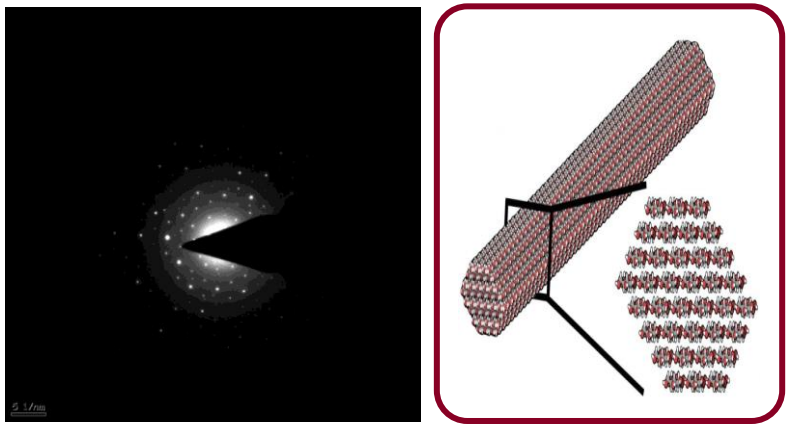
Property of CNCs

- **Nanoscale Size**

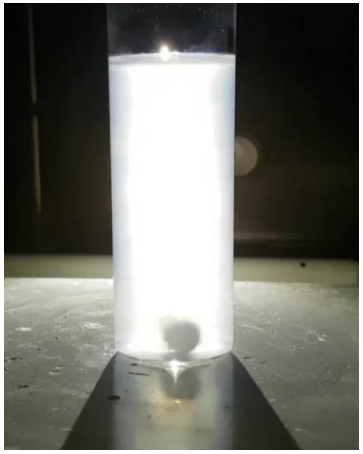




- **Crystallinity**



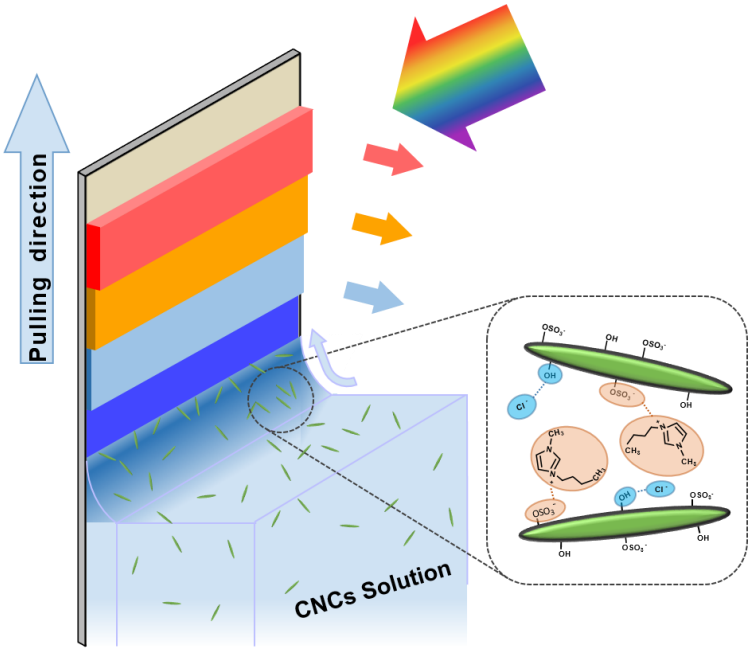
- **Iridescence**



Lagerwall, Jan PF, et al. *NPG Asia Materials* 6, 80 (2014).

- Prepared rod-like CNCs have property of crystallinity and helical self-assembly properties

CNC Films – Dip and Pull Method

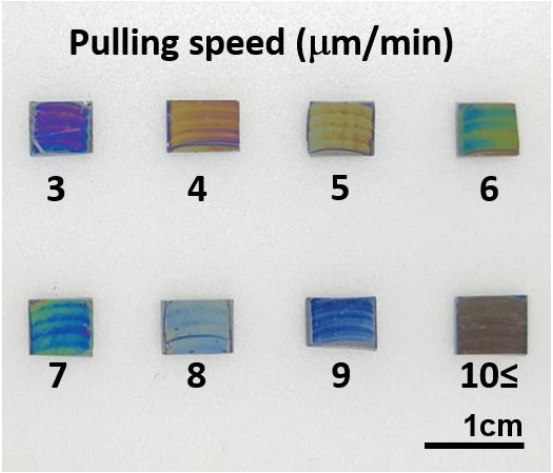


- **Experiment setup**

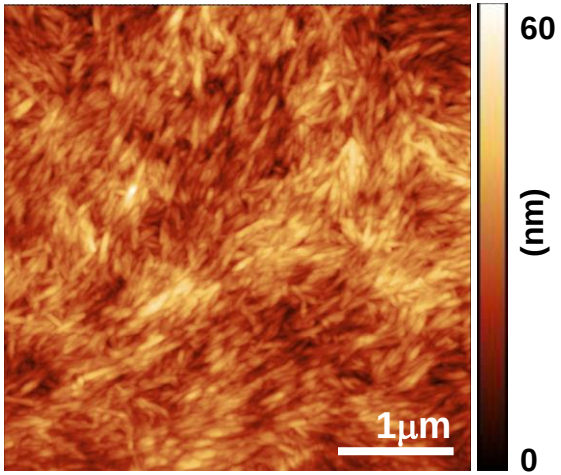
- **Schematic of the fabrication of the CNCs-based color film.**
- **Ionic liquid (BimimCl) interacts among CNCs as described in insert figure.**
- **The substrate was extracted in slowly controlled manner from the ionic CNCs solution.**
- **According to the speed, the thickness of CNC films and their reflection were varied.**

CNC films – Surface & Cross-sectional view

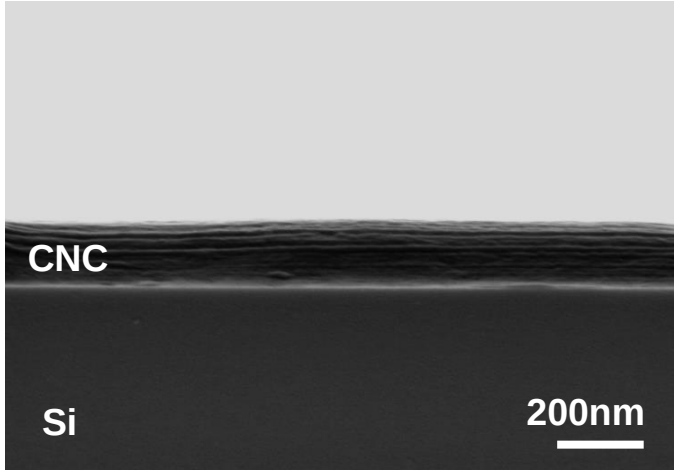
- Optic image of CNC films



- AFM surface topograph



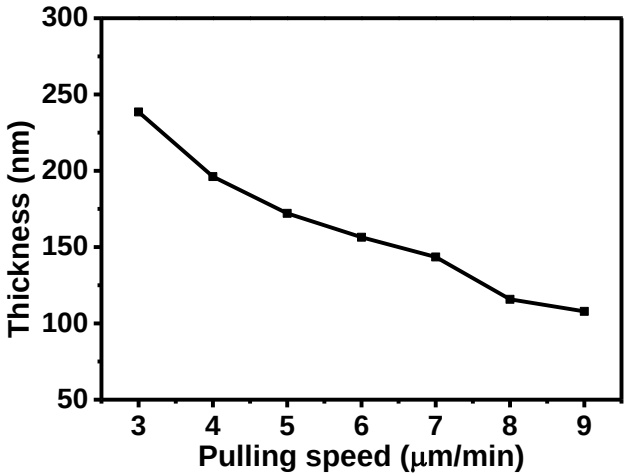
- Side view of SEM image



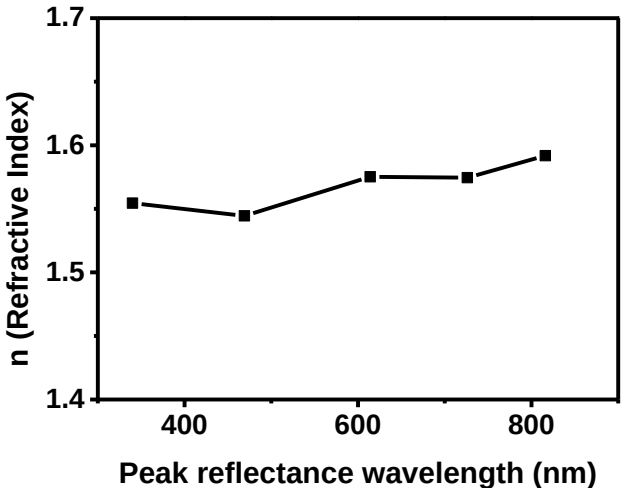
- AFM images of the film showed localized alignment.
- SEM Side view image of CNC-based colored film showed layered structure.

CNC films – Thickness & Refractive index

- AFM height measure

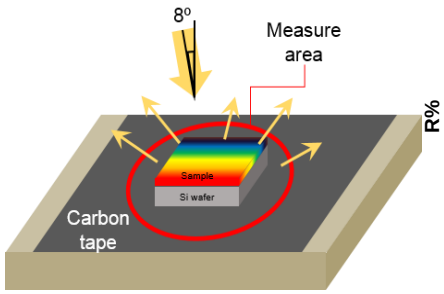


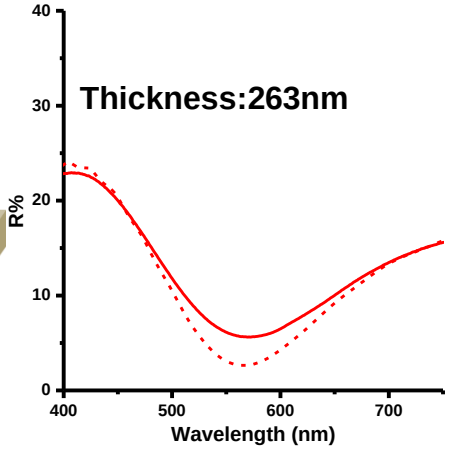
- Ellipsometry (Refractive index)

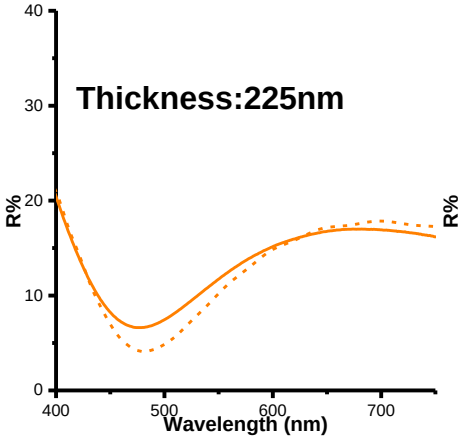


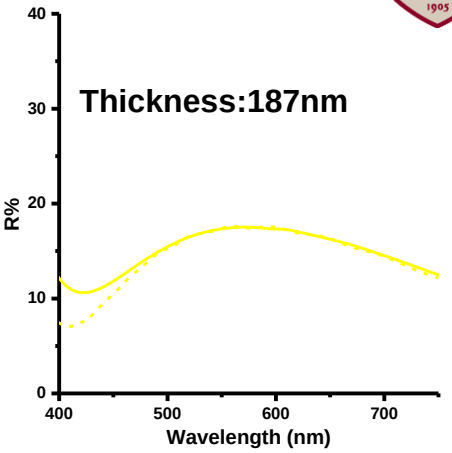
- The thickness was controlled by pulling speed during assembly process.
- The colors were controlled by modulating the pulling speed during assembly process.
- Refractive index was constant, regardless of pulling speed

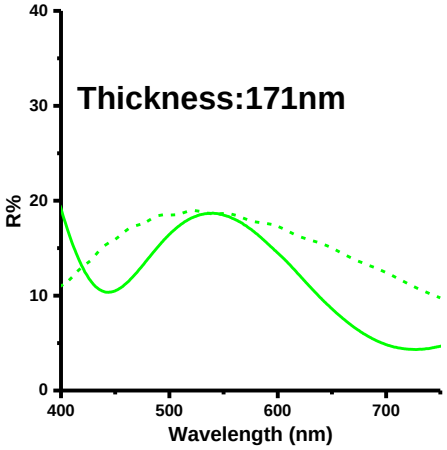
CNC films – Thin film model simulation (FDTD)

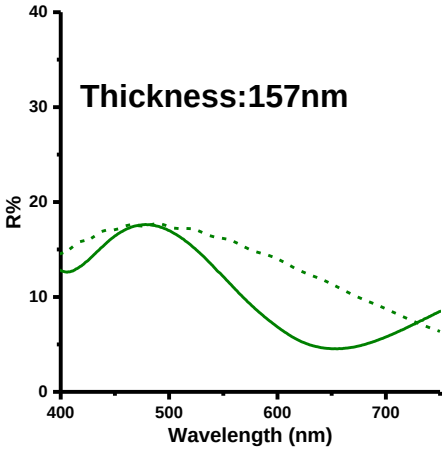


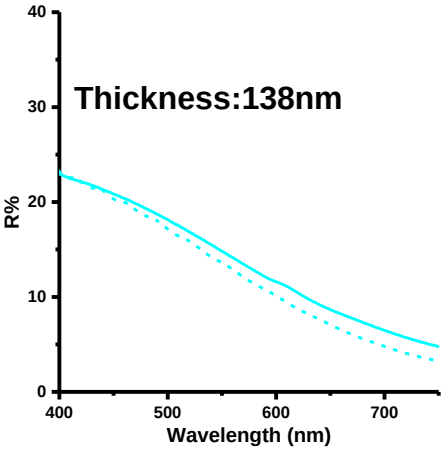


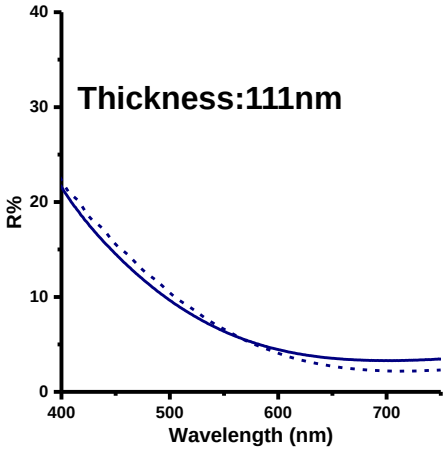










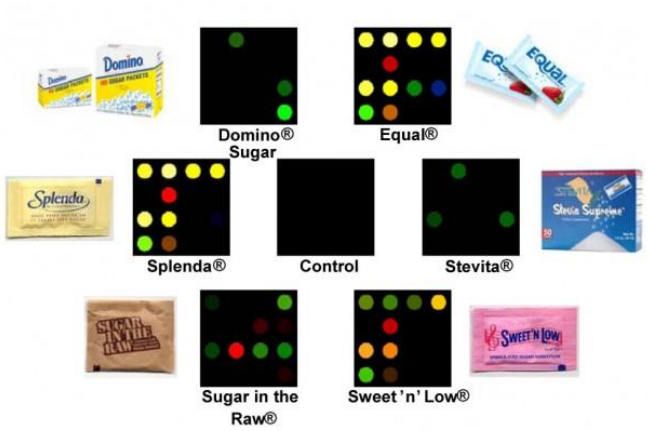


- **For constant refractive index, and increasing thickness as a variable, we fitted reflectance of the CNC films with FDTD**
- **Deviation was caused by roughness of the surface**

Part Ⅱ. CNC color film gas sensors for aldehyde gas detection

Nanocellulose based structural color gas sensor

Nanocellulose + structural color Gas sensor



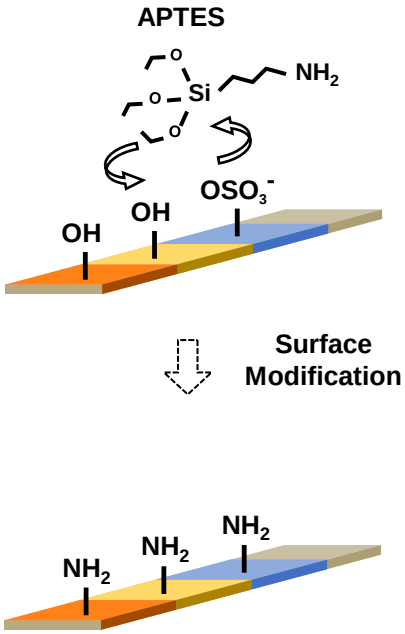
Chemical reaction induced
mechanical structural change

Disposable convenient gas sensor

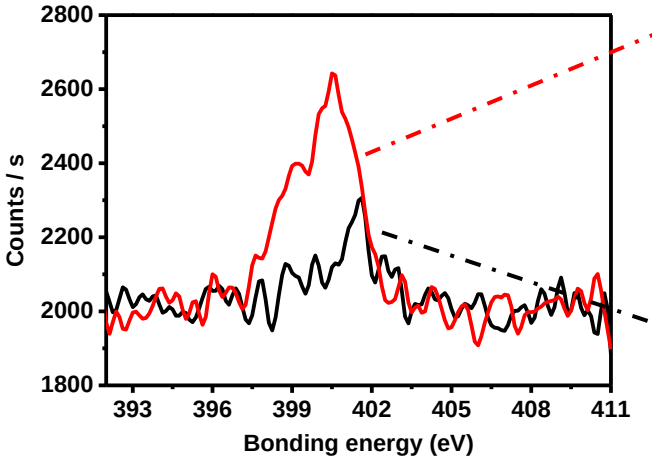
- Environmental friendly
- Low cost
- Degradable device

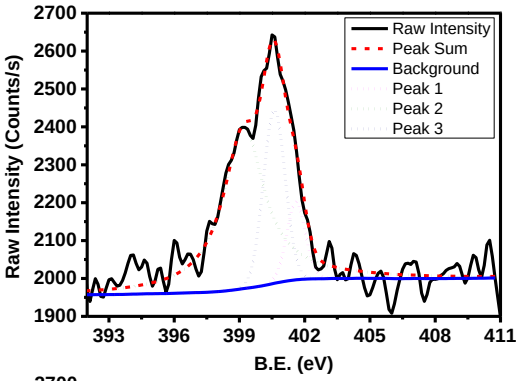
(UIUC, Suslick Group)

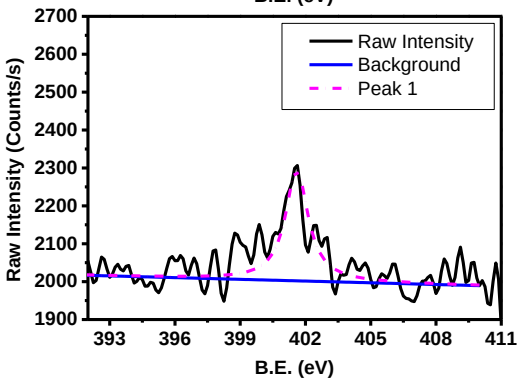
CNC sensors – Surface modification



- XPS analysis
  (Before and after surface modification)

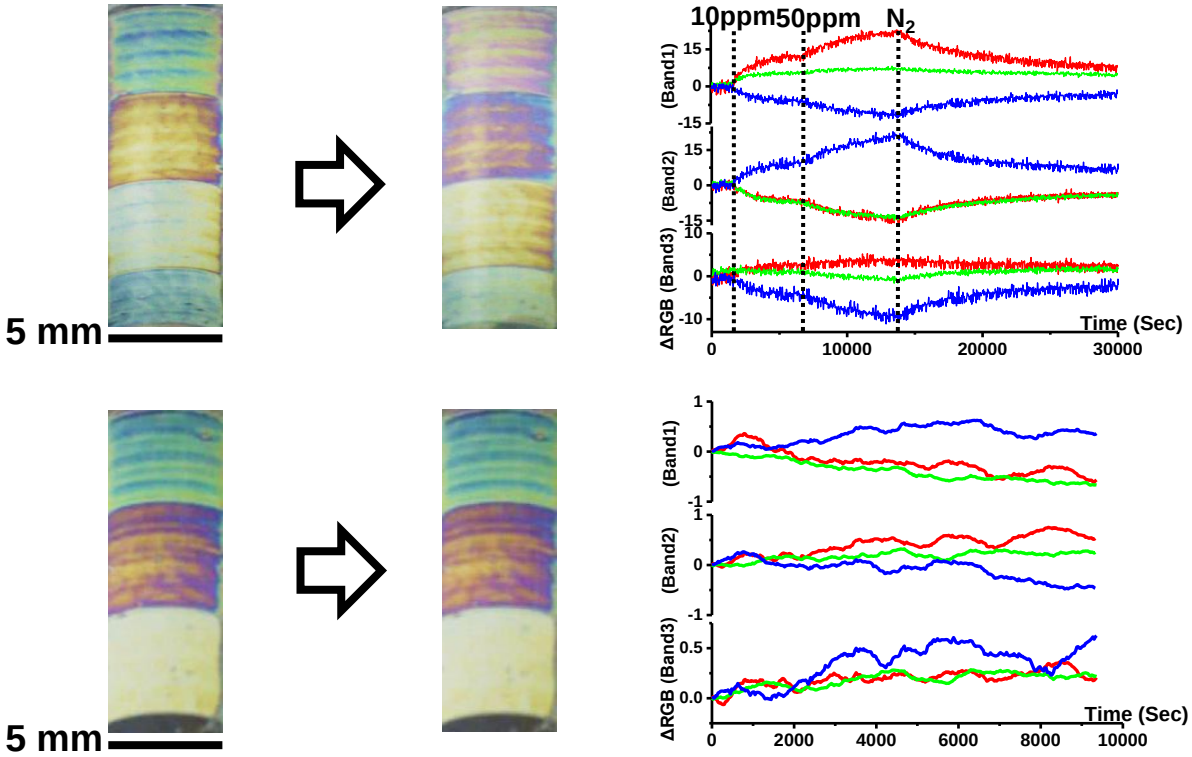






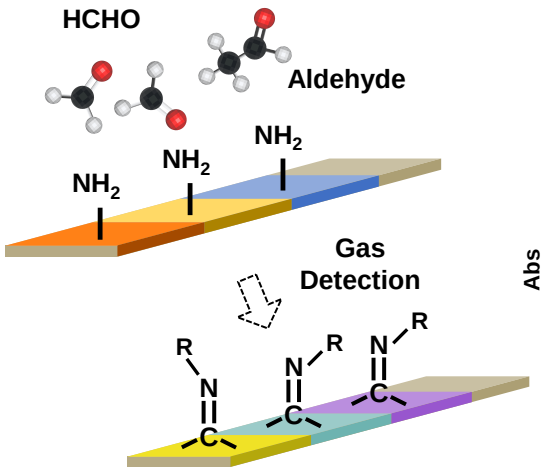
- **At surface of the CNC color film, hydroxyl functional groups were substituted with amine functional groups.**
- **The increasement indicates that numerous APTES molecules attached to the surface of the CNCs thin film, at XPS bonding energy range of 399–401 eV. (S1 shell electron of nitrogen).**

CNC sensors – Detection with color shifting

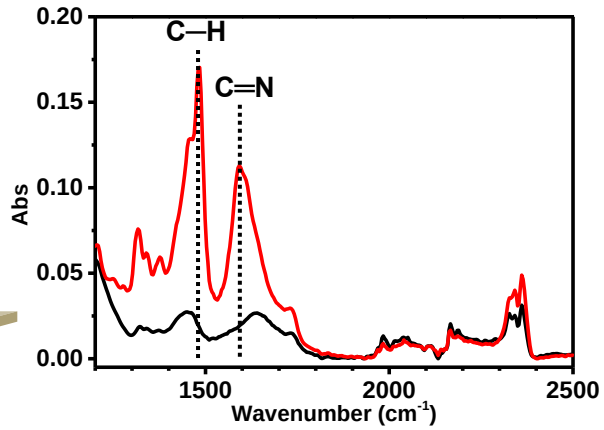


- **Optical images of film's and trend of RGB color intensity change during target gas detection and recovery (formaldehyde, N2 ambient).**
- **No amine functionalization → no color change**

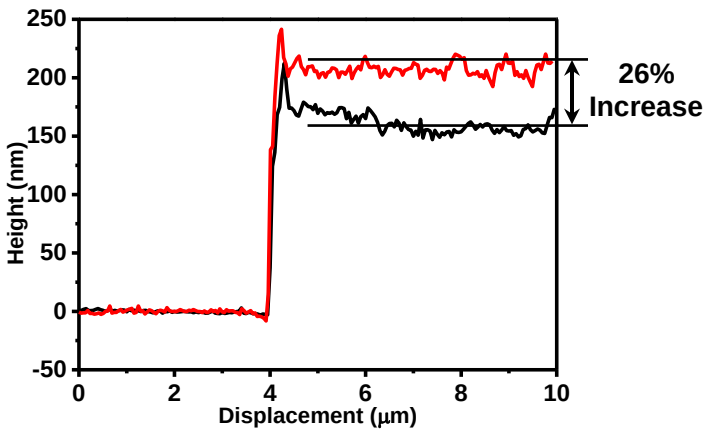
CNC sensors – Chemical & mechanical analysis



- FTIR
(Before and after aldehyde sensing)



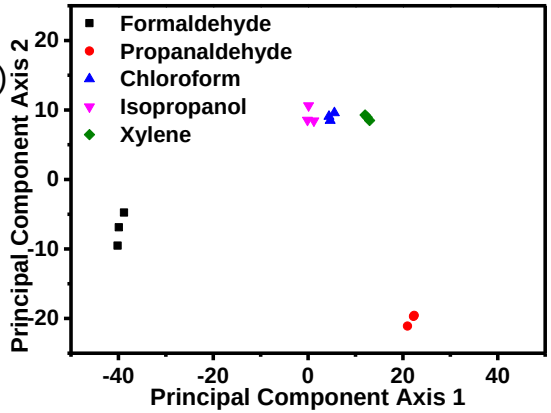
- AFM Height measure
(Before and after aldehyde sensing)



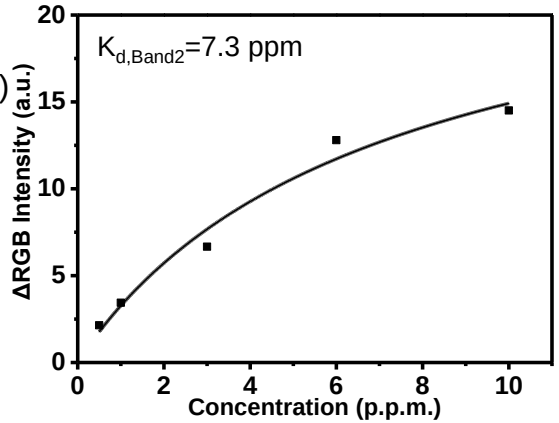
- **Increase in C-H and C=N bond indicates etherification between aldehyde and amine functionalized CNCs surface.**
- **Chemical reaction caused mechanical swelling of CNCs bundles, so the thickness of the CNC film increased and the colors of the CNC film changed.**

CNC sensors – Sensitivity & Selectivity

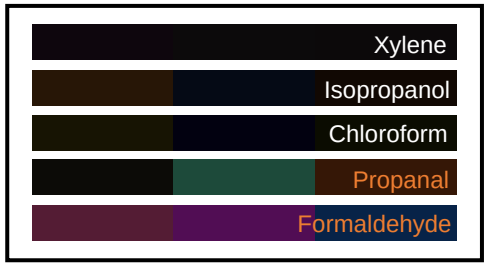
• PCA (selectivity)



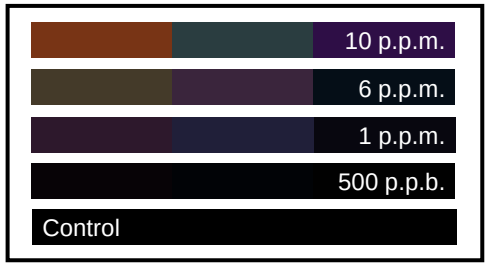
• Hill's equ. (sensitivity)



• ΔRGB visualization (For various gases)



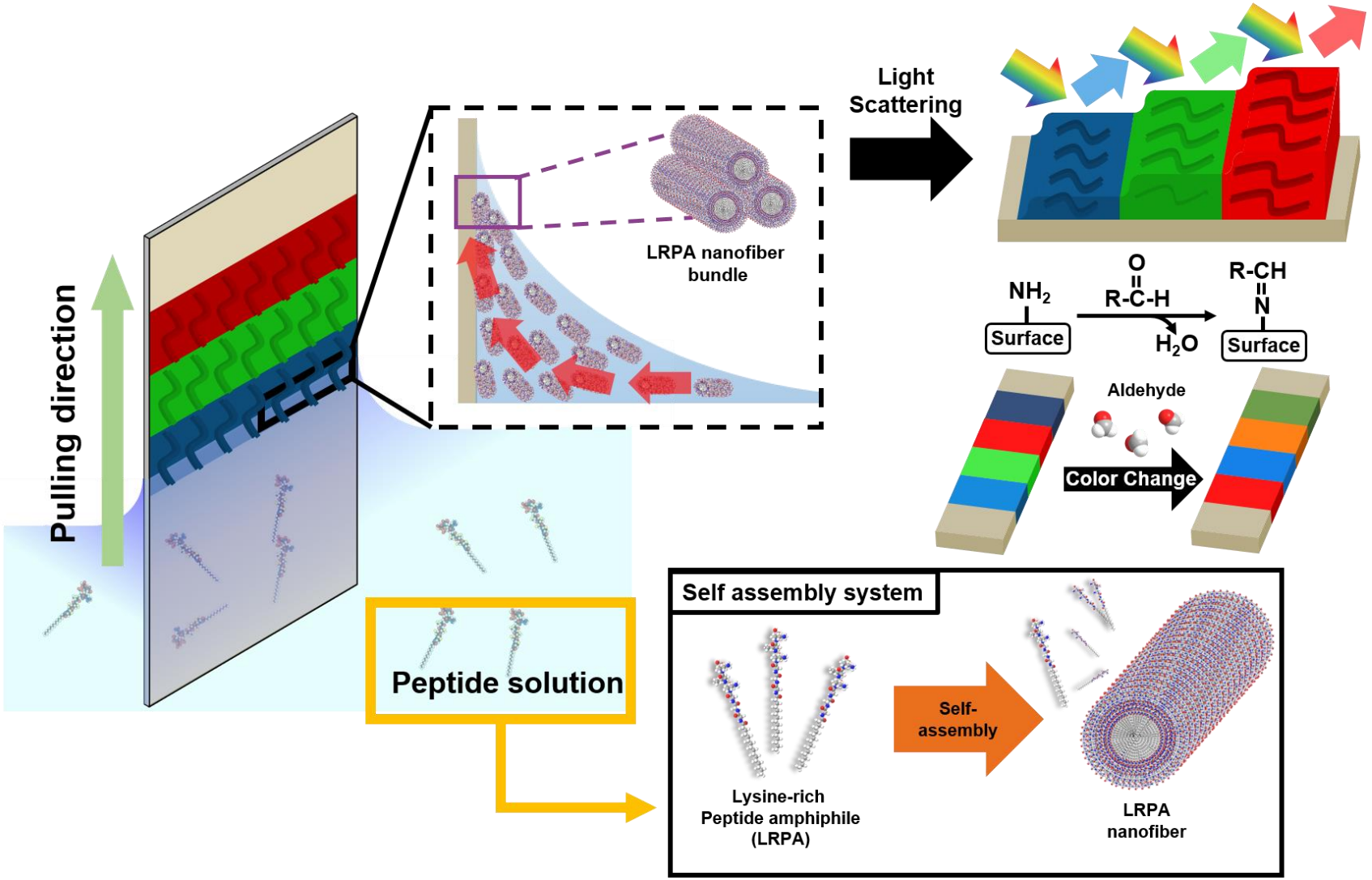
• ΔRGB visualization (For various concentration)



- PCA of color shift reaction enables distinguishing various types of gases
- ΔRGB visualization generally shows the selectivity to aldehyde gas against non-aldehyde gas.
- The dissociation constant K_d (7.3 ppm) shows the sensitivity of the color film sensor quantitively.

Part III. Lysine-rich Peptide Nanowires

Lysine-rich Peptide Amphiphiles (LRPAs)

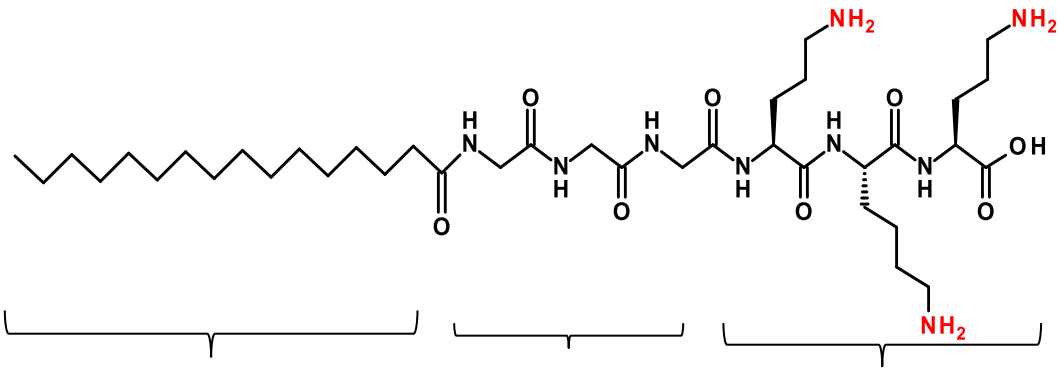


Cowork with Prof. Woojae Chung (SKKU)

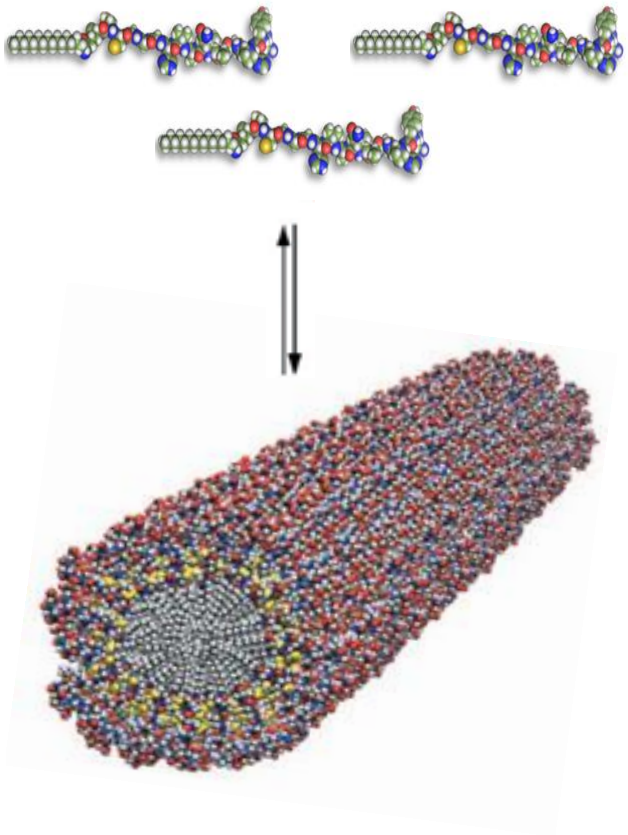
Peptide Amphiphiles

Palmitoyl-GGGKKK [Peptide Amphiphile(PA)]

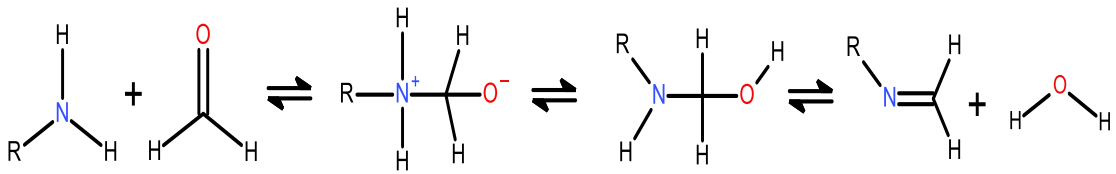
Self-assembling motif + **Aldehyde binding motif**



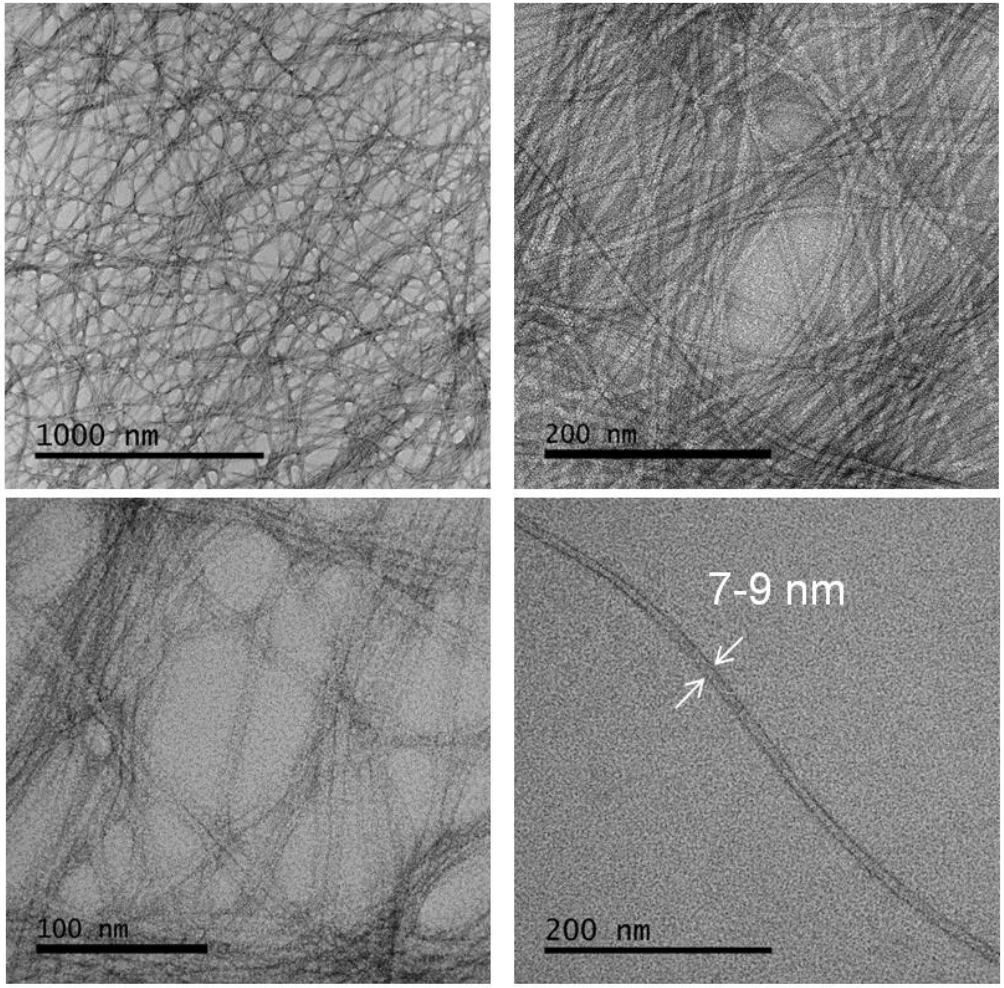
Nanofiber formation by self-assembly

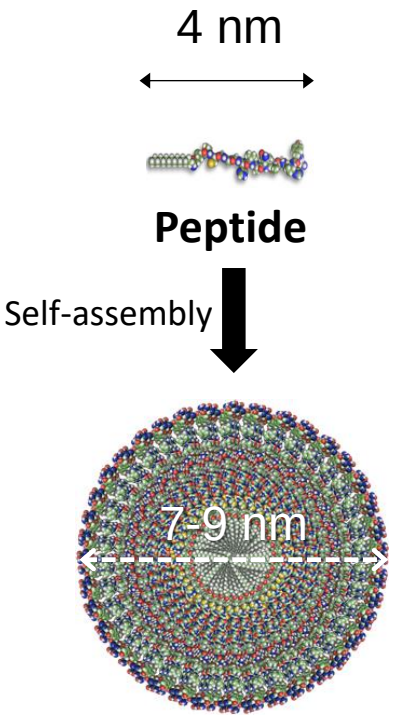


Mechanism of imine formation

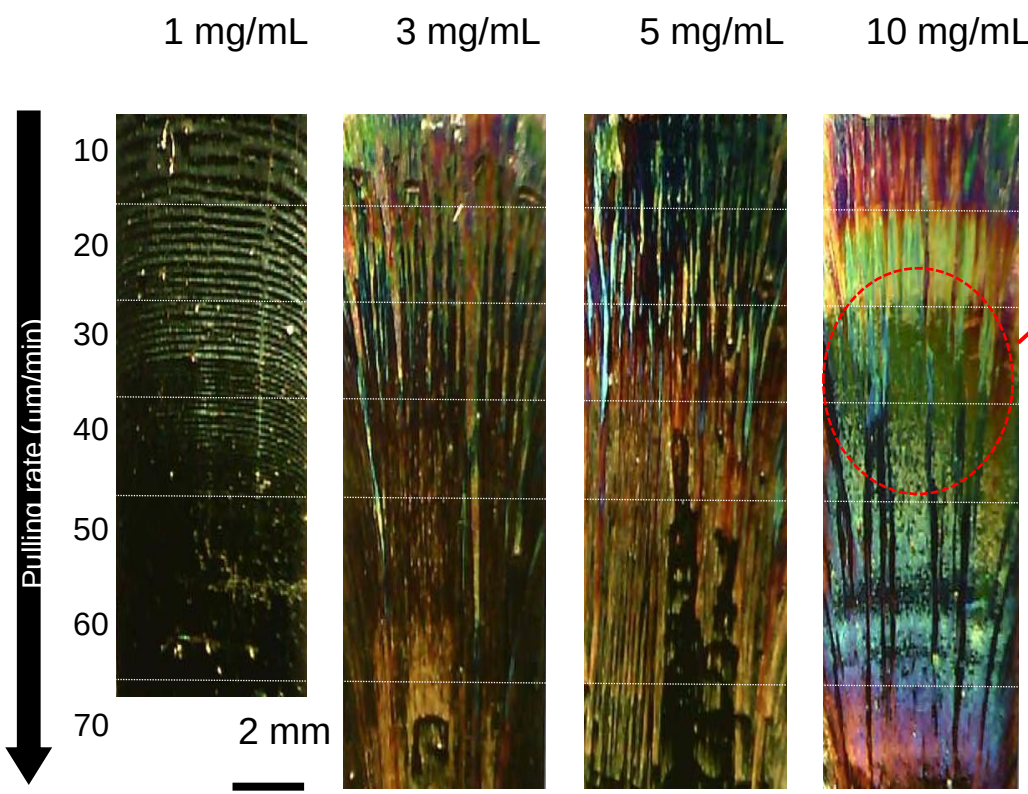


Peptide Nanowires





Fingering Effect: Not Good



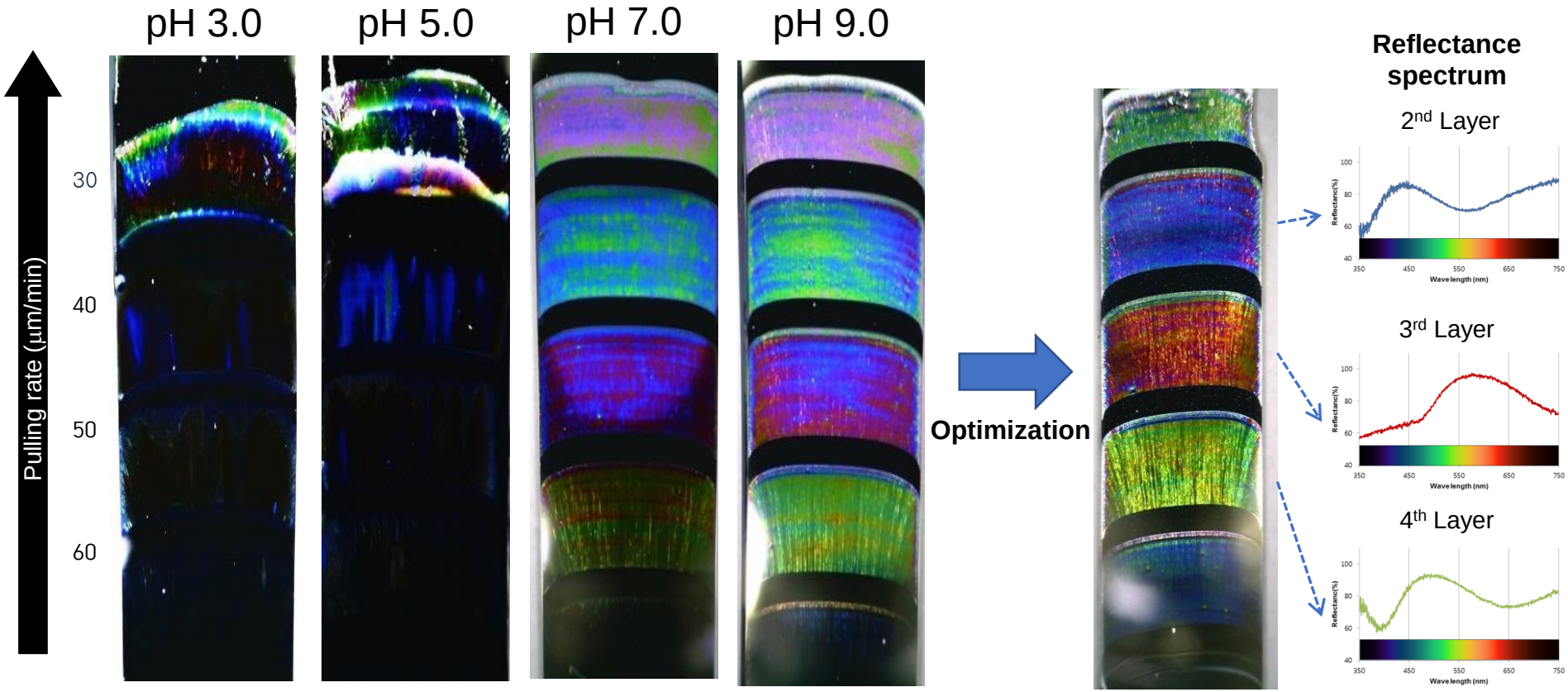
“Fingering effect”

Condition	
Substrate	Gold-coated silicon wafer
Pal-G3K3 Solution	Solvent : DI water Concentration : 1, 3, 5, 10 mg/mL

Factors influencing structural color formation

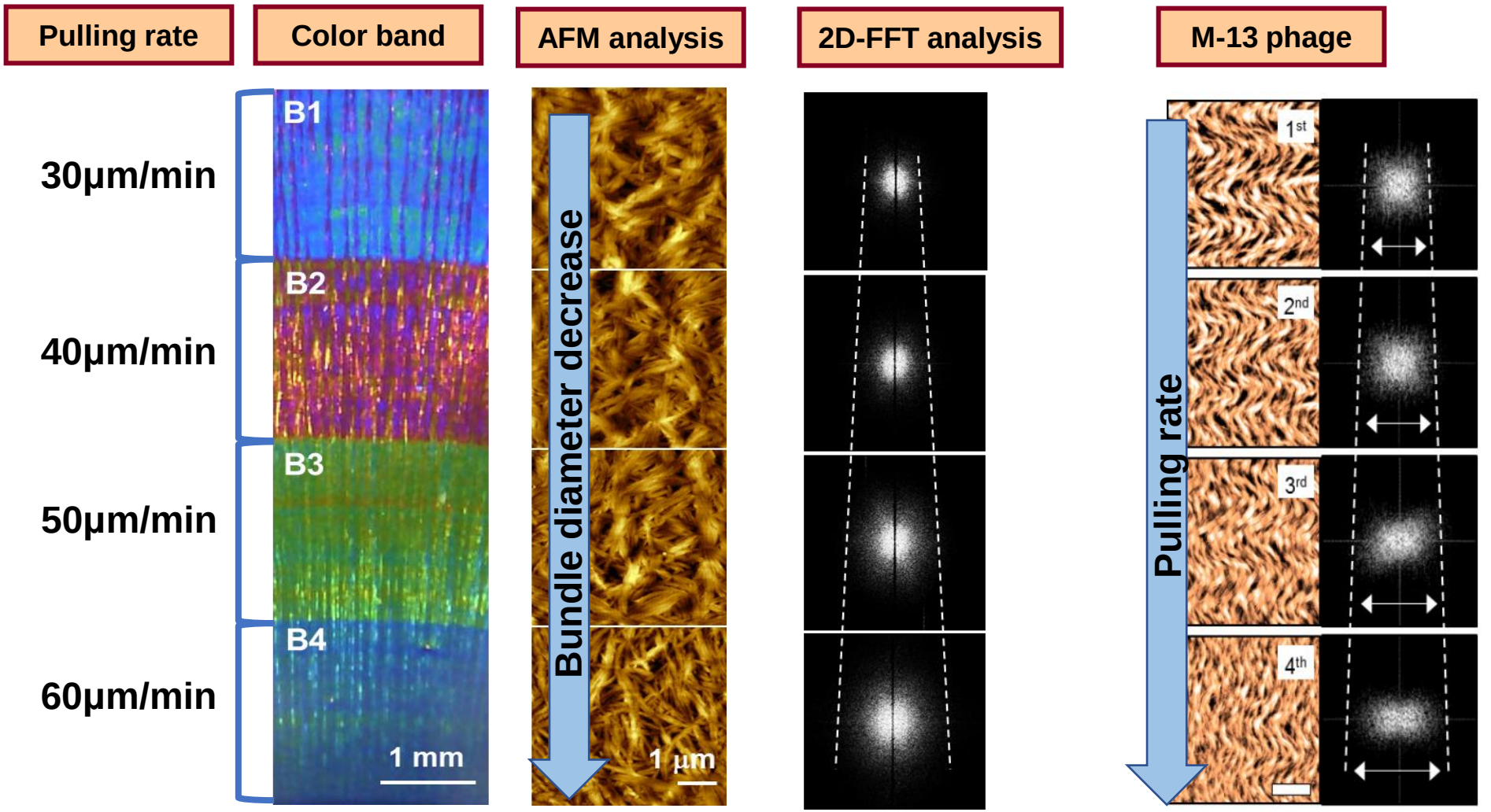
1. Adhesion of Peptide to substrate
   · Substrate surface modification (using thiol or silane chemistry)
2. Interaction between Peptides
   · pH, ionic concentration

Control of pH



Condition	
Substrate	Aluminum-coated silicon wafer
Pal-G3K3 Solution	Solvent : Phosphate buffer (20mM / pH 3, 5, 7, 9) Concentration : 10 mg/mL

Structural Color Matrix Characterization



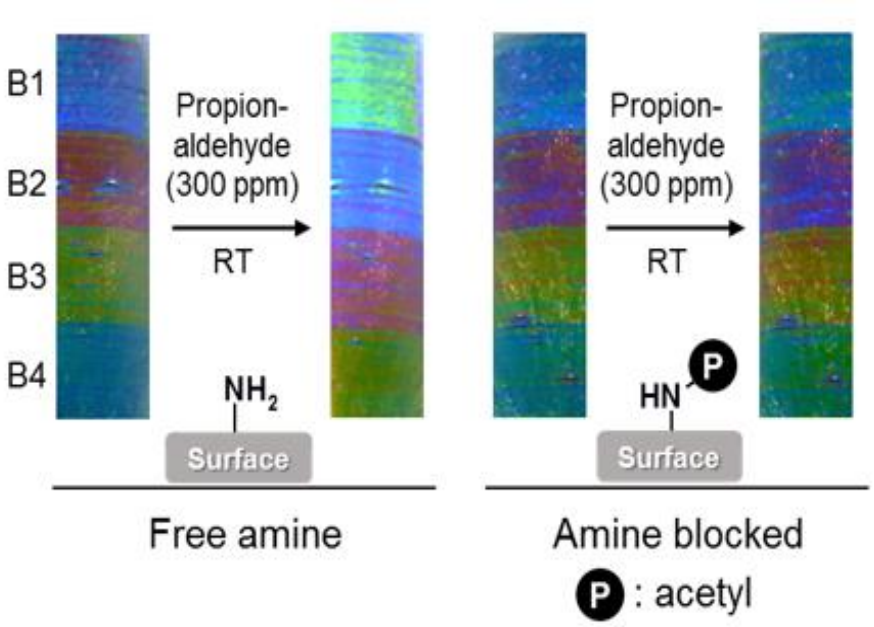
JW Oh, B.Y.Lee et al. ***Nature Communications*** *5,* 3043 (2014)

- **Pulling rate affects on structure of the nanofibers.**

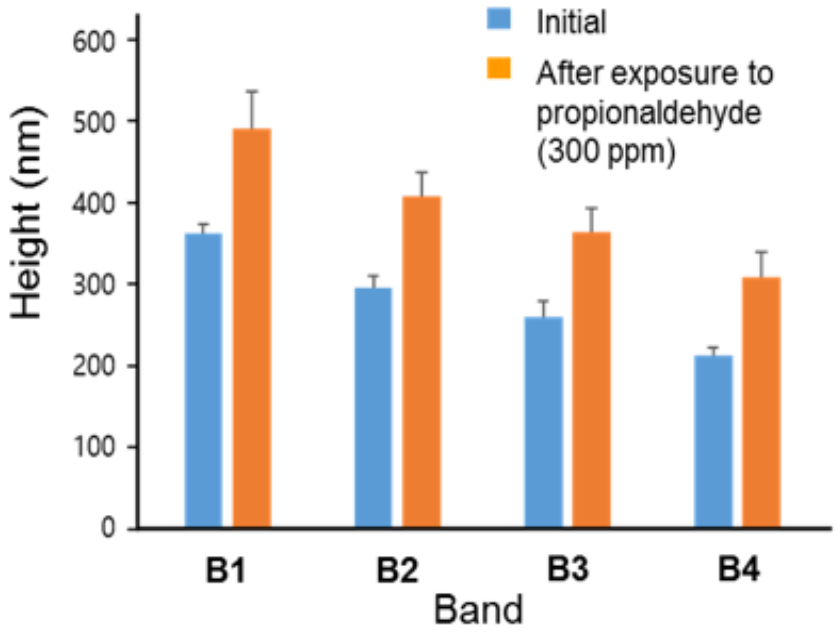
Propanal Gas Detection

Structural Color Change

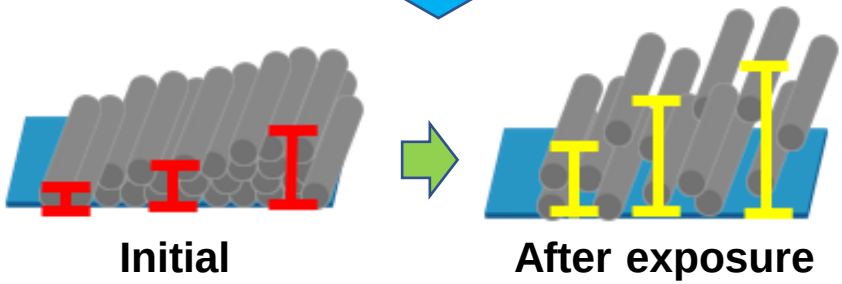
Importance of amino groups



Thickness upon aldehyde exposure



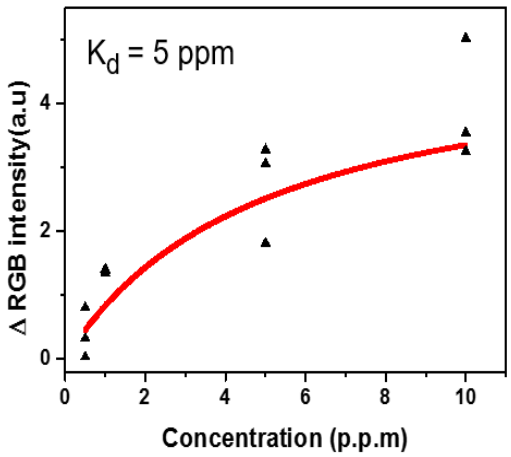
Swelling effect



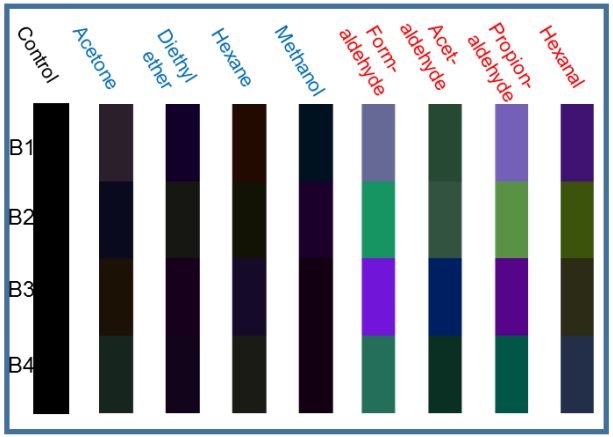
- **After amine blocking(by acetylation) the pattern show inappreciable color changes of propionaldehyde exposure.**
- **Peptide amphiphile-assembled structures showed swelling with thickness increase upon interaction with aldehydes. (profiler)**

Quantitative and Color Change Pattern Analysis

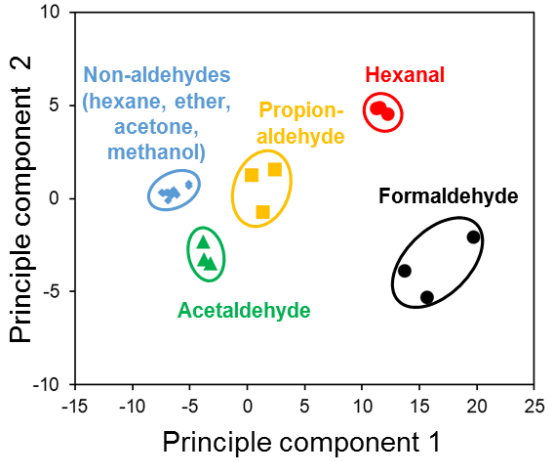
Sensor sensitivity



Aldehyde specific sensor



PCA analysis

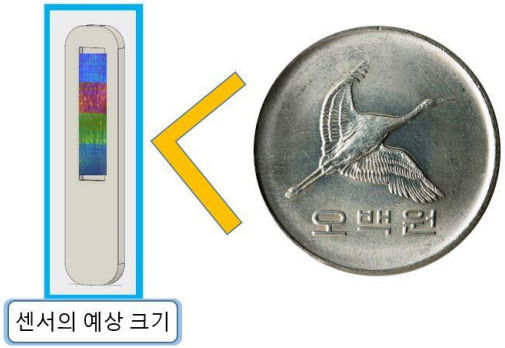


- **Measurement of DRGB between aldehydes and non-aldehydes**
- **2D-PCA analysis shows the separation between aldehydes and non-aldehydes**
- **The results confirmed that peptide color-film sensor has great potential of aldehyde-specific sensor.**

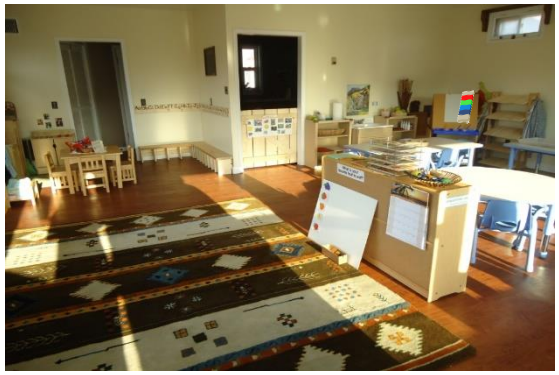
Future Applications

Food Deterioration (~10 ppm)

Industry (2~6 ppm)



Easy to use, Low-cost, Distributed Monitoring



IAQ (~0.2 ppm)

Public Safety (~40 ppb)

Conclusions

- Basic Building Blocks → Structures → Functions
  - Biomimetic
  - Biological
  - Nature-extracted
- Challenges: Efficient Film Fabrication Methods, Large-Area, Repeatability, Quantitative Detection
- **Diverse Applications:**
  - **Gas Detection**
  - **Paper Electronics**
  - **Food Spoilage, etc**

Acknowledgments

- **Students**
  - **Wonbin Song, Gyuyeob Oh, Hyung Soo Kim, Do Hoon Lee**
- **Research Groups**
  - **Prof. Woojae Chung (SKKU)**
  - **Prof. Jinwoo Oh (Pusan National Univ)**
  - **Prof. Seung-Wuk Lee (UC, Berkeley)**

National Research Foundation of Korea

MINISTRY OF ENVIRONMENT

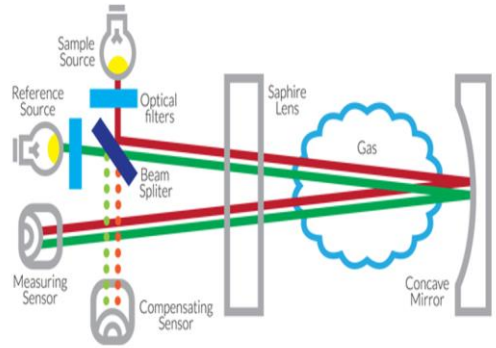
LG Electronics

Thank you for your attention.

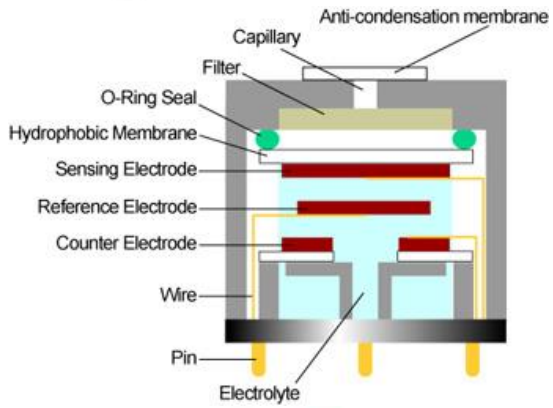
Structural color for sensor application

Conventional gas sensor

Optical
23%



Electro-chemical
52%



Electro-catalytic
23%

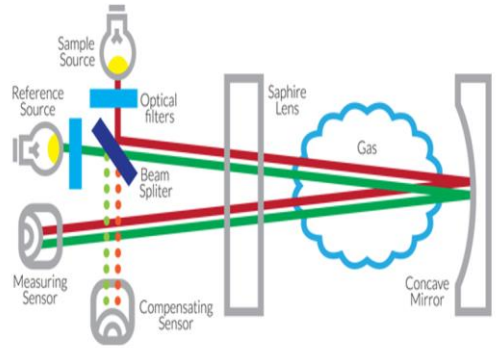
- Toxic chemicals
- Expansive
- Power consumption

https://www.compa.re.kr
Google images “Gas sensors”

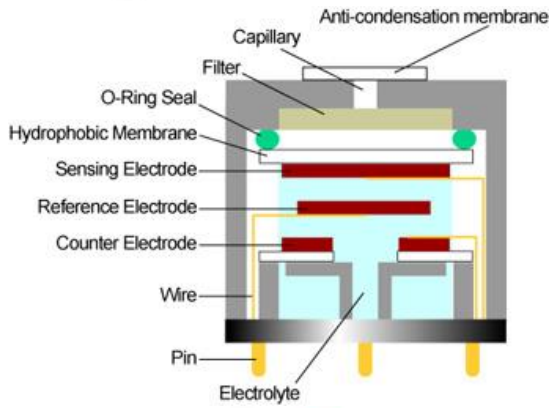
Structural color for sensor application

Conventional gas sensor

Optical
23%



Electro-chemical
52%



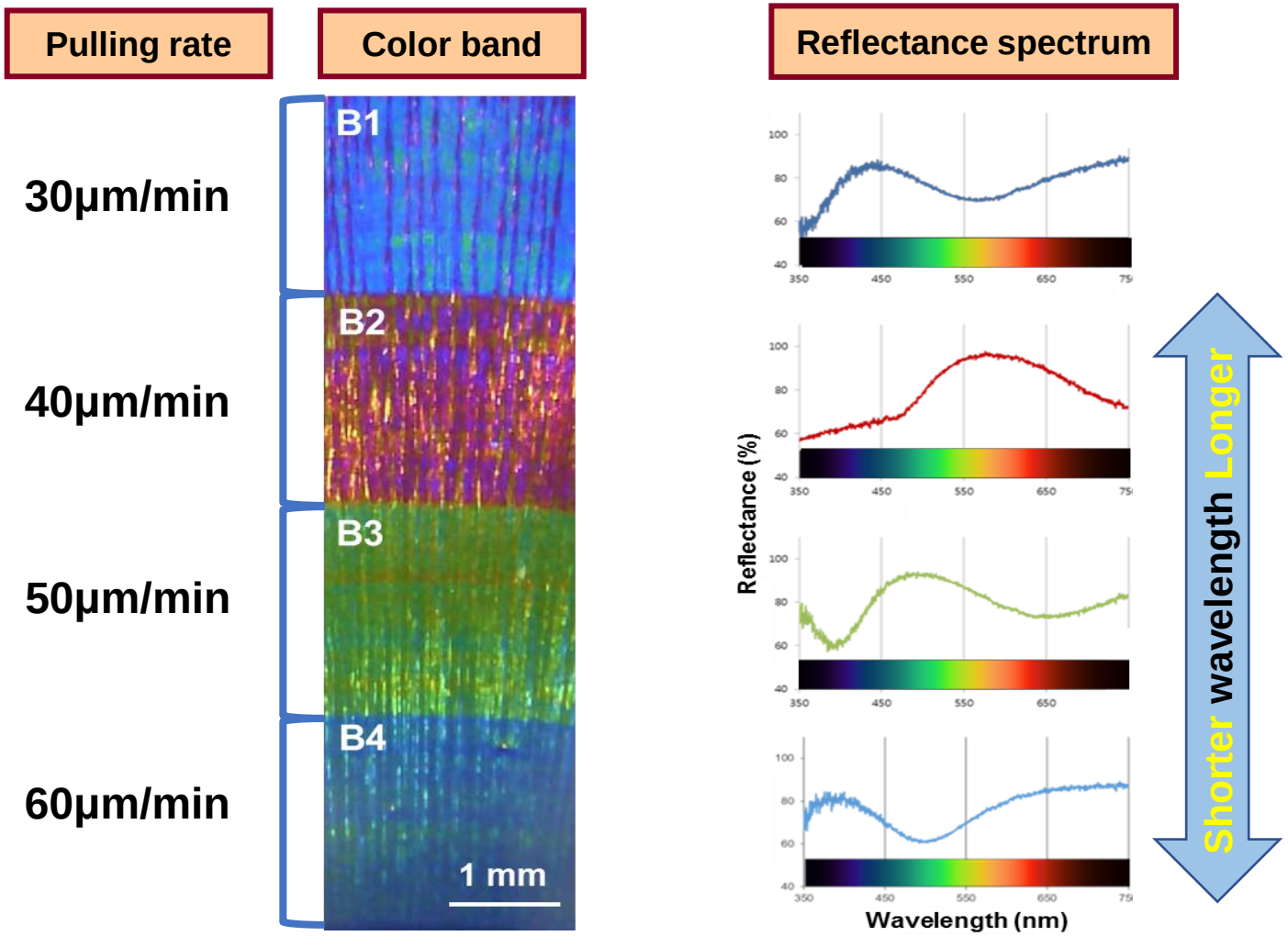
Electro-catalytic
20%

Structural color sensor

- **Simple production**
- **Low price**
- **Power free system**

https://www.compa.re.kr
Google images “Gas sensors”

Structural Color Matrix Characterization

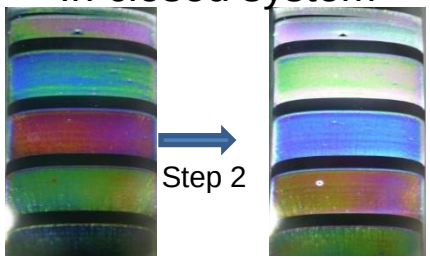


- **The nanofibrous structures with larger diameter exhibited a longer wavelength colors.**

타겟 가스와의 결합 반응 연구

Reversibility

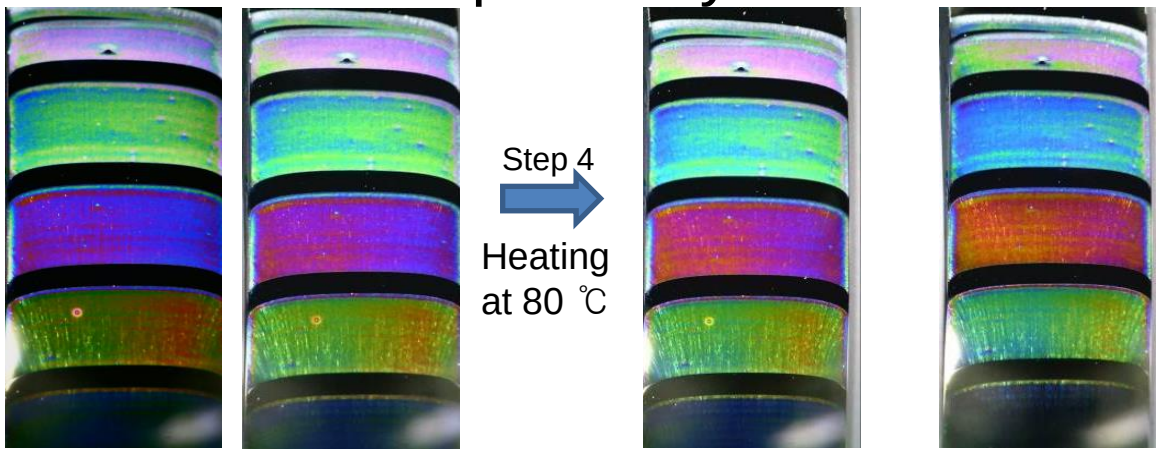
In closed system



Water 15min

Propanal 30min

In opened system



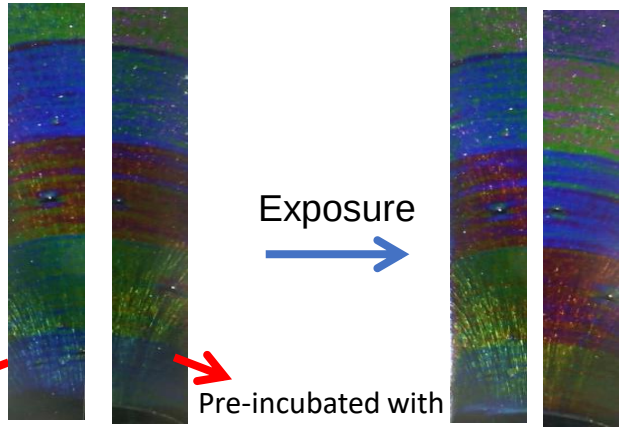
2h

14h

20min

Initial

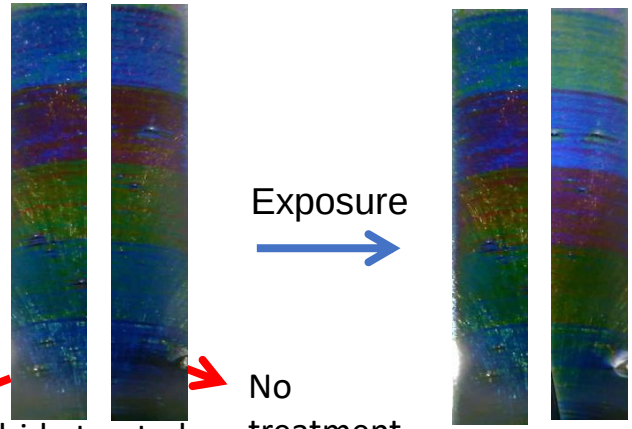
Pre-incubation with water



No treatment

Pre-incubated with water

Amine blocking



Acetic anhydride treated

No treatment

Conclusion

Cellulose nanocrystal colored thin films

- Developed method for tuning color of nanocellulose film utilizing material's unique properties.
- Observed micro/nano structure of the color film and deviation caused by fabrication condition variance.

CNC color film for aldehyde gas sensors

- Developed method for tuning color of nanocellulose film utilizing its unique properties.
- Observed micro/nano structure of the color film and deviation caused by the fabrication condition variance.