Remcho research group

MICRO-TECHNOLOGIES REALIZED

Development of Spiropyran Immobilization and Characterization Protocols for Reversible Photo-Patterning of SiO_2 Surfaces

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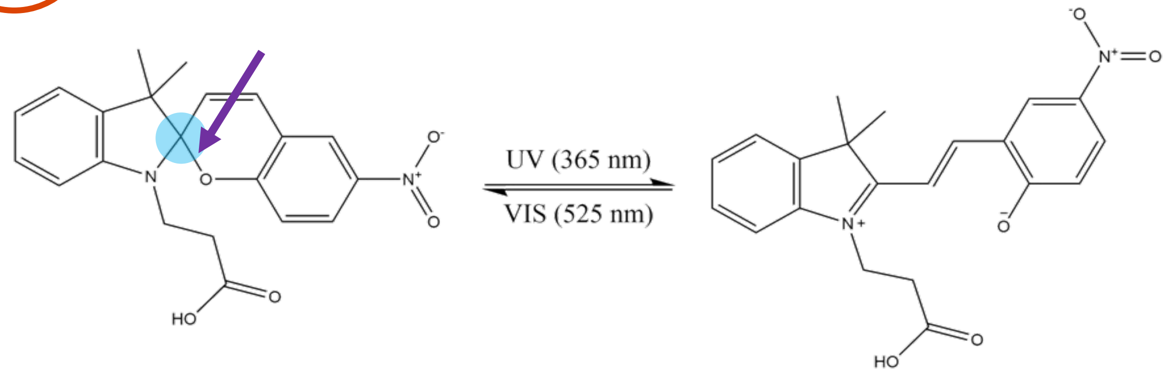
Oregon State University

2023 MRS FALL MEETING & EXHIBIT

50 YEARS

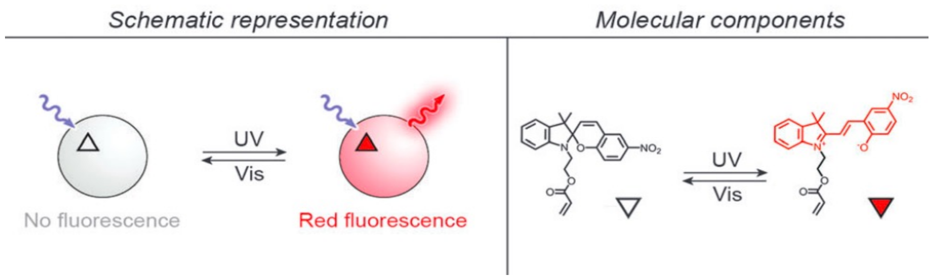
Properties of Spiropyran



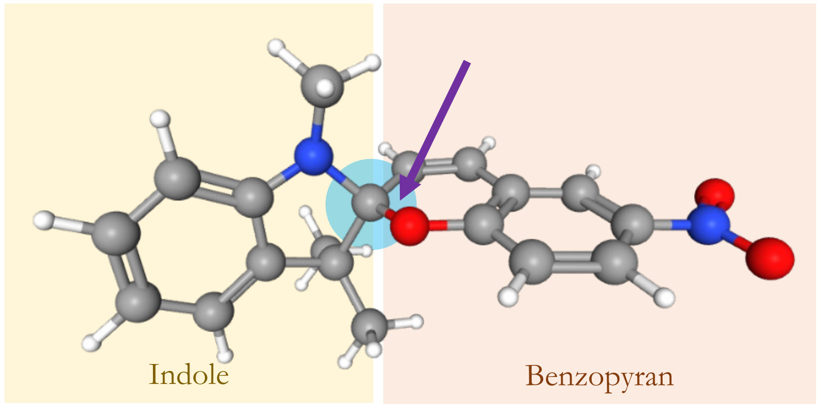
Spiropyran (SP)
hydrophobic, colorless
closed form

Merocyanine (MC)
hydrophilic, purple
open form

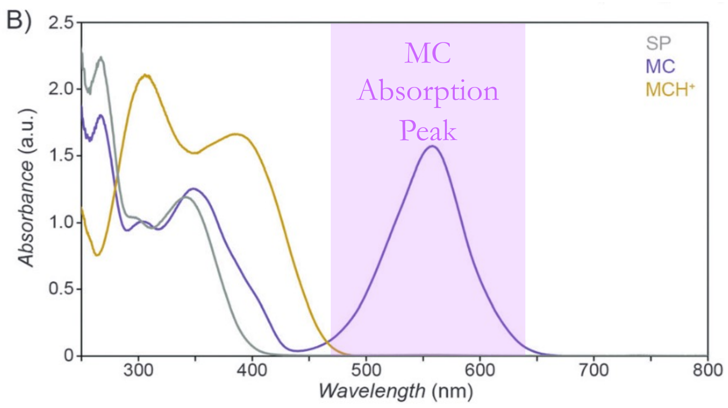
- Photochromism
  - Reversible conversion
  - Triggered by lights



MC form is fluorescent at red 630nm[1]



Chemical structure of a common spiropyran



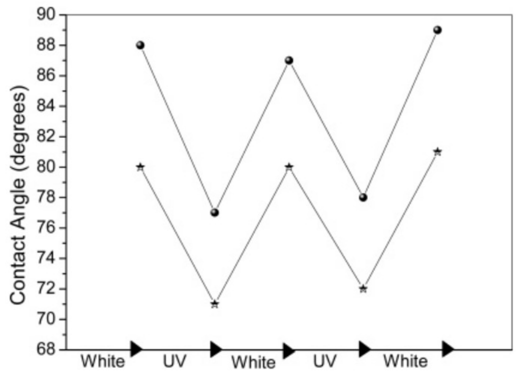
UV-VIS spectra of SP, MC and protonated MC[1]

Sensitive to various stimuli [1]

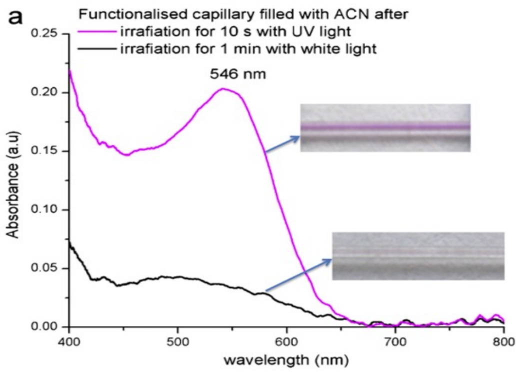
- Light
- Temperature
- pH
- Solvent polarity
- Metal ions
- Redox potential
- Mechanical stress

[1] R. Klajn, “Spiropyran-based dynamic materials,” *Chem. Soc. Rev.*, vol. 43, no. 1, pp. 148–184, 2014, doi: 10.1039/c3cs60181a.

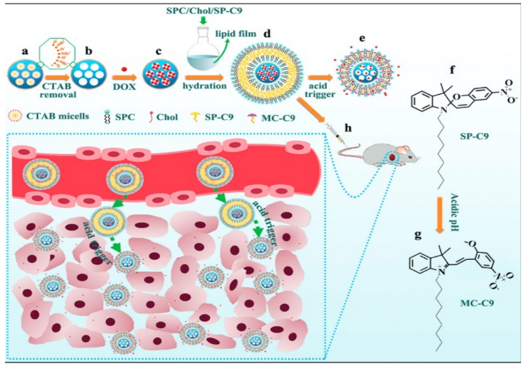
Spiropyran Applications with SiO_2



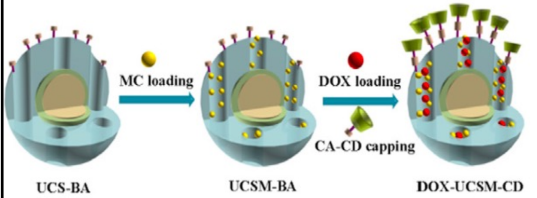
Silicon wafer
Change of contact angle[1]



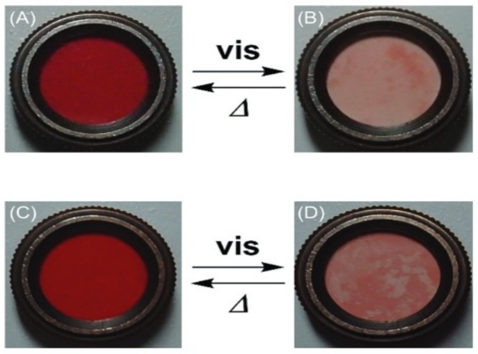
Silica capillary
Capillary-integrated optical sensor[2]



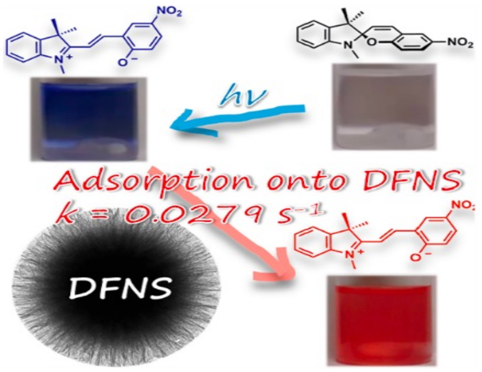
Silica, mesoporous
Size changes (pH); drug delivery[3]



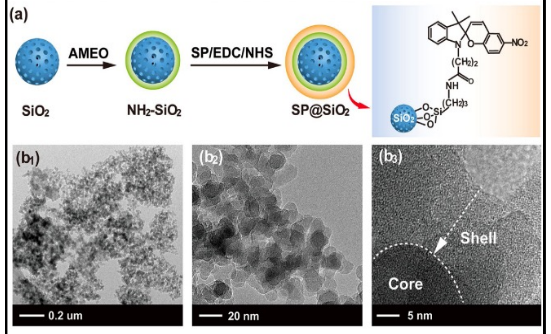
Silica, mesoporous
Ring-opening (pH); drug release[4]



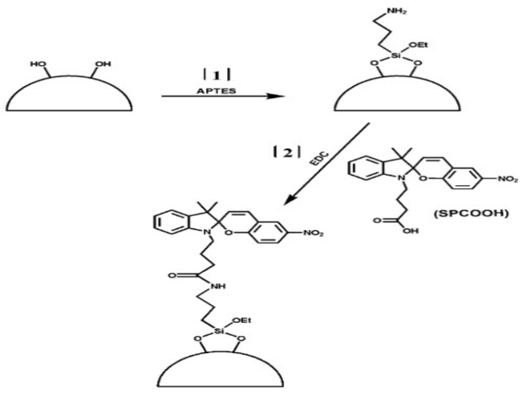
Silica, mesoporous
Pore size affect kinetics[5]



Silica, dendritic fibrous
Photo-induced adsorption[6]



Silica, nanoparticle
Adsorption of fluoride contamination[7]

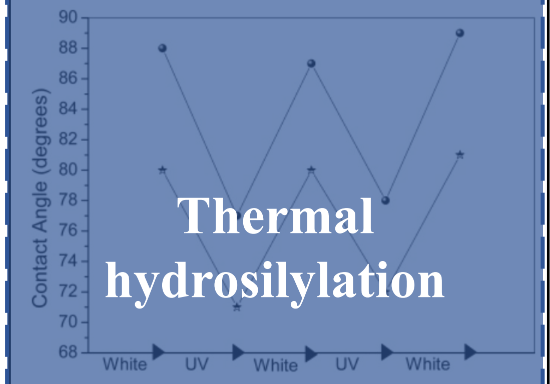


Silica, microbeads
Metal ion extraction[8]

Spiropyran Applications with SiO_2

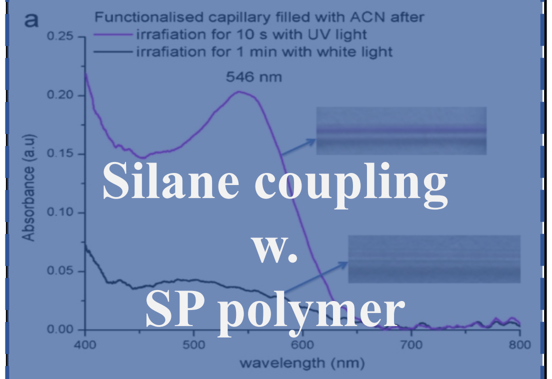
Aim of this work

- Robust immobilization, optimized
- Quick and effective characterization



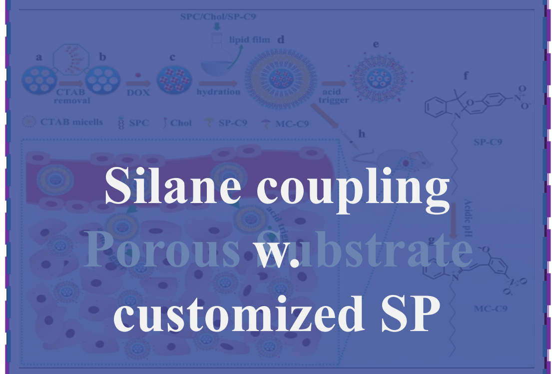
Thermal hydrosilylation

Silicon wafer
Change of contact angle[1]



Silane coupling w. SP polymer

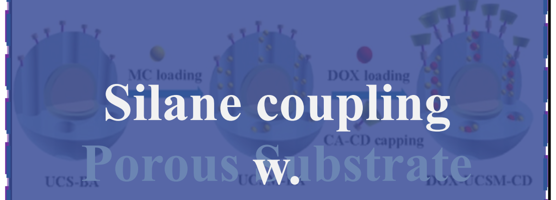
Silica capillary
Capillary-integrated optical sensor[2]



Silane coupling w. customized SP

Porous Substrate

Silica, mesoporous
Size changes (pH); drug delivery [3]



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Non-covalent bonded

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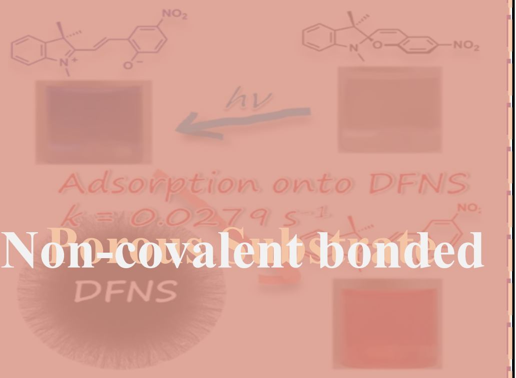

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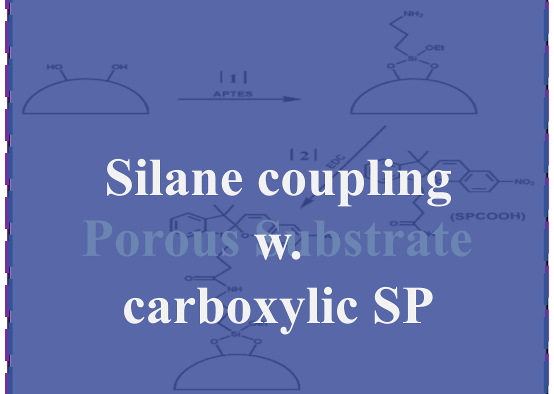
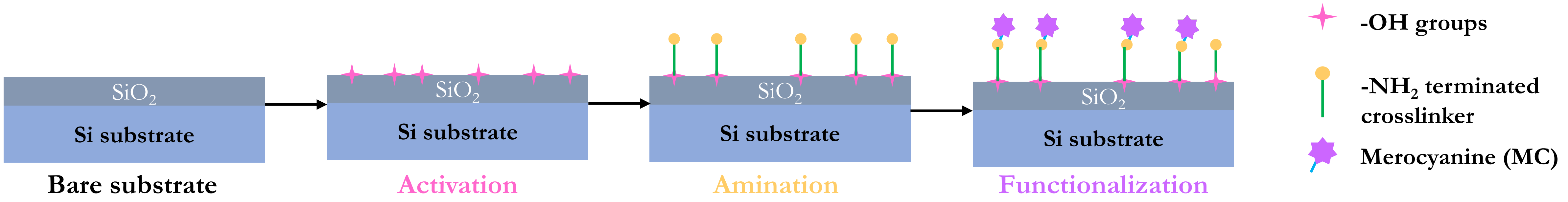


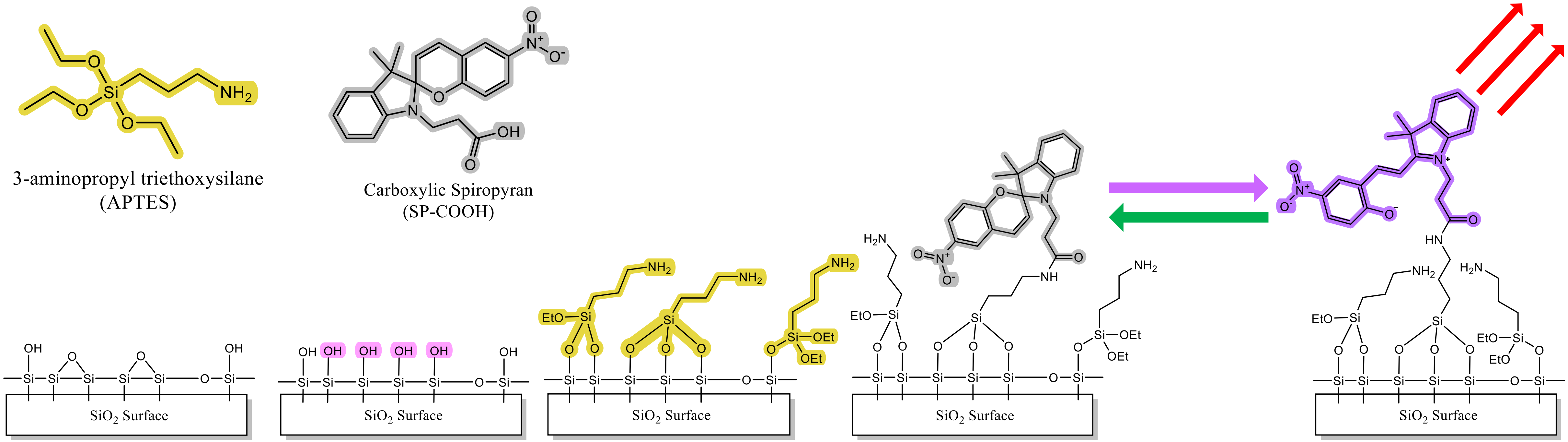
Silane coupling w. carboxylic SP

Porous Substrate

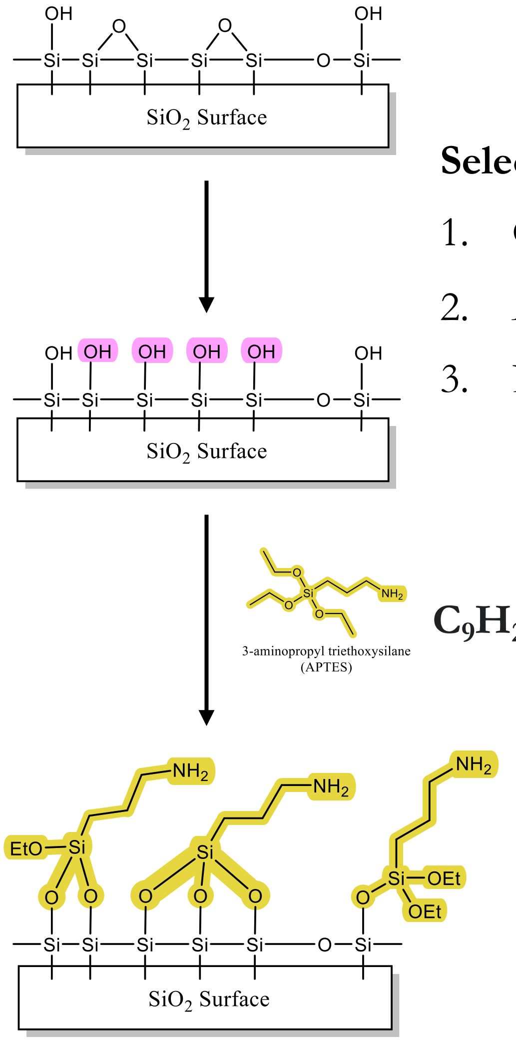
Silica, microbeads
Metal ion extraction [8]

Technical Approach (this work)





Immobilization: effective activation and amination



$C_9H_{23}NO_3Si$

Selected Activation Methods

1. Oxygen plasma treatment
2. Acid treatment (1M HCl)
3. Piranha solution: (H_2SO_4 + H_2O_2)

Surface Atomic Concentration by XPS and Contact Angle

Activation Step

	C 1s	O 1s	Si 2p	Contact Angle
Untreated SiO_2 Surface	2.8%	67.1%	30.1%	60° – 70°
Activated with O_2 plasma	3.8%	67.5%	28.8%	10° – 15°
Activated with HCl	2.8%	67.6%	29.6%	10° – 15°
Activated with H_2SO_4	2.7%	67.6%	29.7%	10° – 15°

Surface Atomic Concentration Table by XPS

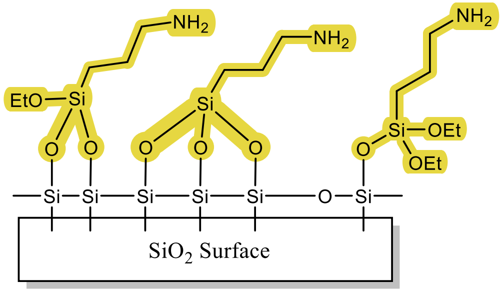
Amination Step

$C_9H_{23}NO_3Si$

Amination Process Condition	C 1s	O 1s	Si 2p	N 1s	% organosilicon*	N : % organosilicon
2% APTES 5min@RT	22.4%	50.7%	24.1%	2.8%	2.7%	1.0
2% APTES 10min@RT	40%	36.9%	18.0%	5.1%	4.7%	1.1

*: from the immobilized APTES

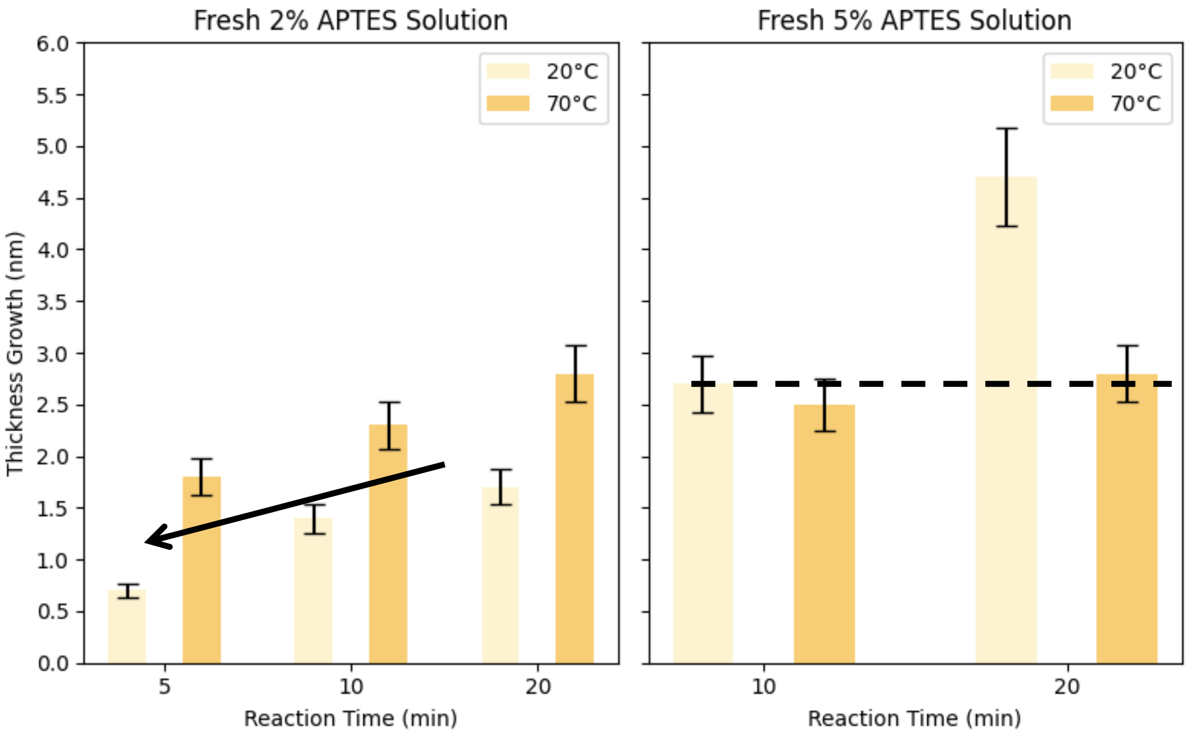
Immobilization: thin layer of APTES amination



Thin layer, ideally mono-layer

Incubation with APTES

- Reaction Time
- Reaction Temperature
- APTES Concentration



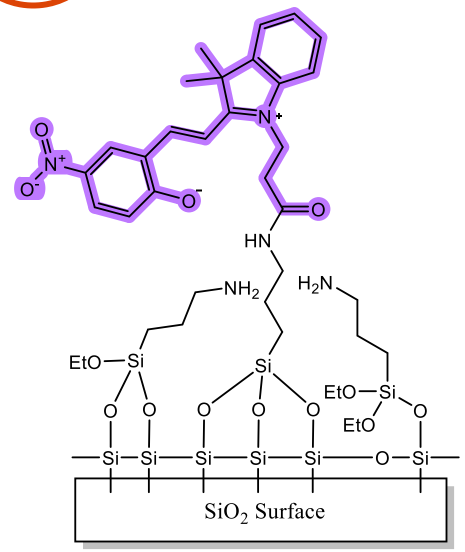
Incident light

Reflected light

Ellipsometry Model

- To reduce self-reaction
  - Freshly prepared APTES solution
  - 2% APTES at room temperature for 5min → **0.5 – 0.7 nm**
- From XPS results, N:% organosilicon is approximately 1:1.
- Together, the results verifies a successful thin layer amination.

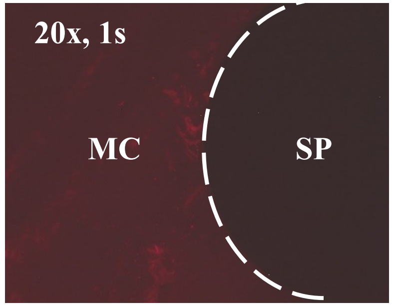
Immobilization: functionalized surface with fluorescence



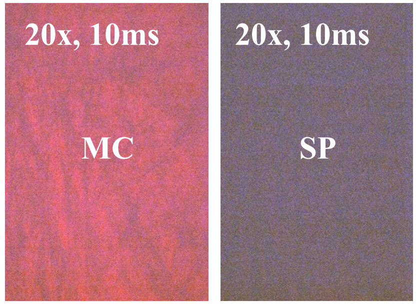
Incubation with SP-COOH and EDC

- EDC-mediated coupling of carboxylic acids and amines

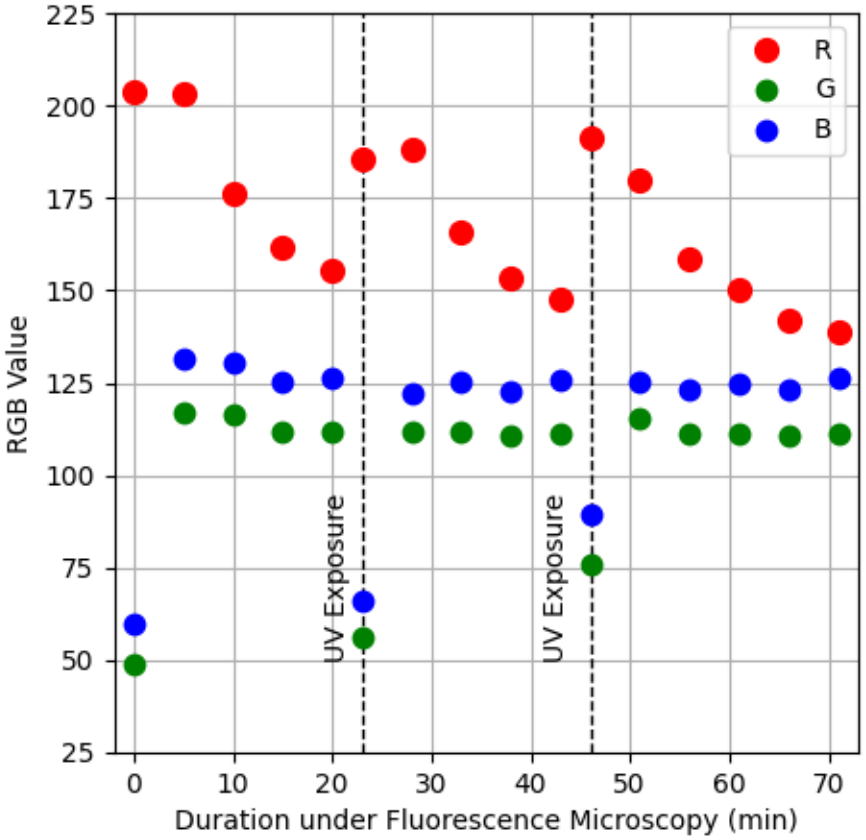
- Extracting RGB value from fluorescence images, taken at setting of 20x, 20ms

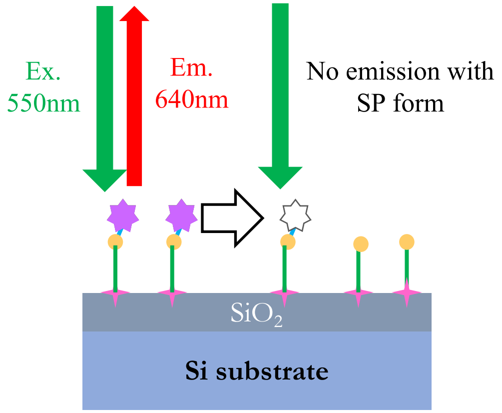


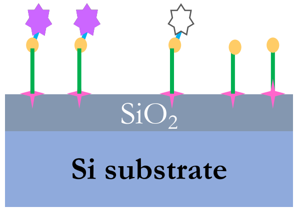
MC-immobilized SiO_2 sample

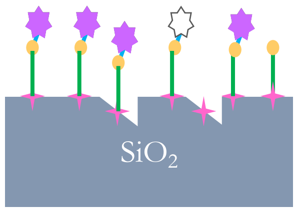


MC-immobilized **glass microfiber** sample







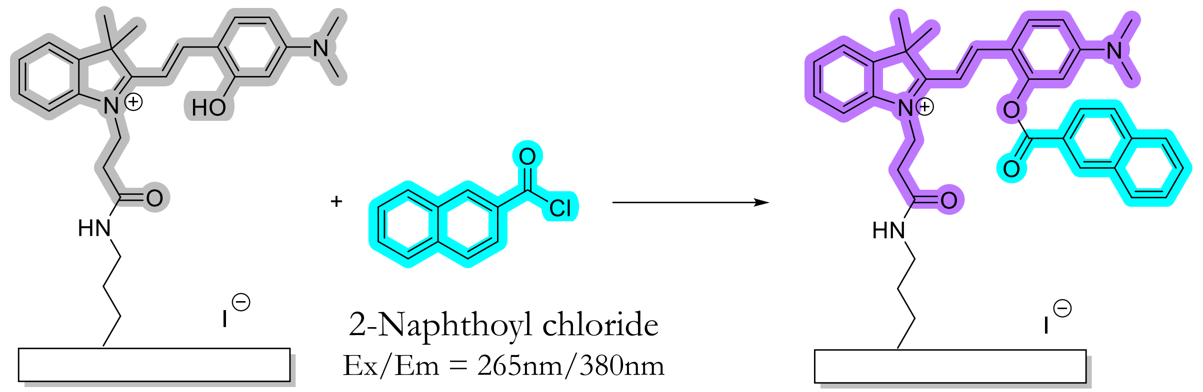


Summary and Future Work

- ✓ Immobilization Protocol
  - ✓ Effective activation
  - ✓ Thin layer amination
  - ✓ Fluorescence functionalization
- ✓ Characterization Protocol: XPS, contact angle, ellipsometry, fluorescence
  - ✓ Change in surface chemistry / surface energy
  - ✓ Controlled thickness growth
  - ✓ Reversible photo-patterning and fluorescence

- ➢ Surface density of functional groups
  - ➢ -OH is limited by surface type
    - ➢ On average, there are 4.9 #/nm^2 OH groups on amorphous silica.[1]

- ➢ Sensitivity of fluorescence detection
  - ➢ Measurement setup
  - ❑ MC-SP conversation
  - ❑ Low quantum yield of MC fluorescence



Proposed Scheme to Further Modify Surfaces
(lock in MC form & enhance fluorescence)

[1] L. T. Zhuravlev, “Concentration of hydroxyl groups on the surface of amorphous silicas,” *Langmuir*, vol. 3, no. 3, pp. 316–318, May 1987, doi: 10.1021/la00075a004.

References

Review Paper

[1] R. Klajn, "Spiropyran-based dynamic materials," *Chem. Soc. Rev.*, vol. 43, no. 1, pp. 148–184, 2014, doi: 10.1039/c3cs60181a.

Spiropyran Application with SiO_2 Surface

[1] D. Dattilo, L. Armelao, G. Fois, G. Mistura, and M. Maggini, "Wetting Properties of Flat and Porous Silicon Surfaces Coated with a Spiropyran," p. 6, 2007, doi: 10.1021/la7024878.

[2] L. Florea, A. Hennart, D. Diamond, and F. Benito-Lopez, "Synthesis and characterisation of spiropyran-polymer brushes in micro-capillaries: Towards an integrated optical sensor for continuous flow analysis," *Sensors and Actuators B: Chemical*, vol. 175, pp. 92–99, Dec. 2012, doi: 10.1016/j.snb.2011.12.055.

[3] Y. He *et al.*, "pH-Responsive size-shrinkable mesoporous silica-based nanocarriers for improving tumor penetration and therapeutic efficacy," *Nanoscale*, vol. 14, no. 4, pp. 1271–1284, 2022, doi: 10.1039/D1NR07513F.

[4] R. Han, S. Wu, K. Tang, and Y. Hou, "Facilitating drug release in mesoporous silica coated upconversion nanoparticles by photoacid assistance upon near-infrared irradiation," *Advanced Powder Technology*, vol. 31, no. 9, pp. 3860–3866, Sep. 2020, doi: 10.1016/j.apt.2020.07.025.

[5] T. Yamaguchi, N. N. Leelaphattharaphan, H. Shin, and M. Ogawa, "Acceleration of photochromism and negative photochromism by the interactions with mesoporous silicas," *Photochem Photobiol Sci*, vol. 18, no. 7, pp. 1742–1749, Jul. 2019, doi: 10.1039/c9pp00081j.

[6] T. Yamaguchi, A. Maity, V. Polshettiwar, and M. Ogawa, "Photochromism of a Spiropyran in the Presence of a Dendritic Fibrous Nanosilica; Simultaneous Photochemical Reaction and Adsorption," *J. Phys. Chem. A*, vol. 121, no. 42, pp. 8080–8085, Oct. 2017, doi: 10.1021/acs.jpca.7b08466.

[7] X. Guan, M. He, J. Chang, Z. Wang, Z. Chen, and H. Fan, "Photo-controllability of fluoride remediation by spiropyran-functionalized mesoporous silica powder," *Journal of Environmental Chemical Engineering*, vol. 9, no. 1, p. 104655, Feb. 2021, doi: 10.1016/j.jece.2020.104655.

[8] S. Scarmagnani *et al.*, "Photoreversible ion-binding using spiropyran modified silica microbeads," *IJNM*, vol. 5, no. 1/2, p. 38, 2010, doi: 10.1504/ijnm.2010.029921.

Limitation on –OH Surface Density

[1] L. T. Zhuravlev, "Concentration of hydroxyl groups on the surface of amorphous silicas," *Langmuir*, vol. 3, no. 3, pp. 316–318, May 1987, doi: 10.1021/la00075a004.

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Q & A

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THANK YOU

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