Photo-responsive materials
Capabilities and Perspectives
July 2014

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Photo-responsive hydrogels

less hydrophilic

more hydrophilic

spontaneous in H₂O

white light

Spontaneous in H₂O

White light
Microstructures preparation

mask

glass slide

spacer (PSA, PSA/PMMA)

glass slide

monomer cocktail
Hydrogels microstructures

1 mol NIPAM
5% Acrylic acid
1% acrylated-Spiropyran
3% MBIS
1% PBPO
Polymerization solvent
Micro-patterned hydrogels

Hydrogel microstructures covalently attached to glass substrates were photo-polymerised through micro-patterned masks using white light.

- Circular masks of 1mm diameter.
- Hydrogel height: 60µm.
- Polymerisation time: 10-20 seconds.
Photo-responsive hydrogels
Photo-responsive hydrogels
1\textsuperscript{st} Irradiation Cycle
Multiple Irradiation Cycles

![Graph showing multiple irradiation cycles over time.](image-url)
Valve applications
Micro-valve fabrication and working principle

1. 250um gel disks polymerised around pillar using mask
2. 250um
3. 250um
Surfactant-driven vehicles

Chemotactic Droplets
Controlled-release of surfactants

A

B

C

D

NaOH $10^{-2}$ M (pH = 12)  

HCl $10^{-2}$ M (pH = 2)
Video 2:

Speed X 2
Multiple Chemotactic Droplets

Speed X 2
Photo-activated chemopropulsion
Speed \approx 100 \, \mu m \, s^{-1}

Speed \times 4

1 \, cm
Perspectives

[Diagram showing a system with ionic liquid, polymer, protonated merocyanine (MC-H+), spiropyran, non-protonated cationic surfactant (water insoluble species), protonated cationic surfactant (water soluble species).]

[Sequence of images A, B, C, D showing the direction of movement in a process.]
Optical Sensors in Microfluidics

Optical Sensors

Microfluidics
Polyaniline functionalised micro-capillaries and micro-fluidic channels

- pH sensing
- ammonia sensing
- diffusion study
Polyaniline Nanofibres

- low cost, easy synthesis
- reversible acid-base doping-dedoping chemistry
- environmental stability

Polyaniline-coated micro-capillaries for ammonia sensing

Micro-capillary functionalisation

Polyaniline-coated micro-capillaries for ammonia sensing
Doping dedoping properties

Ammonia sensing

Micro-chip fabrication

✓ PDMS is poured onto master mold, cured at 80°C for 1 h and removed from mold.

✓ PDMS and glass slide are treated with oxygen plasma.

✓ PDMS and glass slide are brought together.

L. Yu, C.M. Li, Y. Liu et al. / Lab Chip, 9 (2009), 1243–1247.
Micro-channels

500µm x 1000µm

1000µm x 100µm

45µm x 50µm
Fast Response

pH sensing in continuous flow

Dedoping process

Emeraldine Salt (ES) ↔ Emeraldine Base (EB)

pH sensing in continuous flow

Dynamic pH sensing

NaOH $10^{-2}$ M

HCl $10^{-2}$ M
pH gradient sensing

pH gradient sensing

Study of diffusion process
Spiropyran polymeric brushes functionalised micro-capillaries

- ON/OFF sensing
- solvent sensing
- metal ion sensing
Spiropyran

A: Spiropyran SP (closed, colorless)

B: Merocyanine MC (open, colored)
2. Spiropyran-Based Polymers

Most protocols for the incorporation of SP units into polymer matrices generally involve polymerisation of derivatised SP monomers or copolymerisation of these species with compatible monomeric units, where the SP moiety can be introduced as side chain or as a part of the main polymer chain.

Other methods include non-covalent doping/entrapment of SP derivatives within various polymer matrices or functionalisation of pre-formed polymers with SP pendant groups.

A number of examples of SP-based polymer most often presented in recent literature are described in Table 1 and comprise a series of homo- and co-polymers obtained through various polymerisation techniques: radical polymerisation, atom-transfer radical polymerisation (ATRP), ring-opening metathesis polymerisation (ROMP) and photo-polymerisation, among others. Other types of polymers in which the SP is included as a pendant group post-polymerisation or simply used as a dopant are also presented. Table 1 gives an overview of polymers containing SP where the emphasis is on their structure. SP polymeric systems can be used for a variety of applications, showing that by combining the key advantages of the SP moiety with the smart engineering of SP-based polymers, new materials with designed macroscopic properties can be obtained. Various types of SP polymers have been designed in order to acquire photo-control over specific characteristics of the material like permeability towards different analytes, wettability, sensing behaviour, actuation and electrical properties or to visualise mechanical stress.

3. Photo-Modulated Wettability

The wettability of surfaces depends on both, the surface chemistry and the surface morphology, in particular, on the micro-structures of the surface. Having the possibility to...

Our Approach

- polymer brushes
- high loading of spiropyran molecule
- 3D arrangement

Micro-capillary: Convenient platform for rapid analysis and detection

Advantages

- act as a mechanical support for the optically sensitive layer
- represents an optical waveguide structure
- suitable for real-time continuous flow analysis
- requires very small volume of analyte
Characterisation

Solvatochromic Behaviour

- In solution

- Polymeric brushes
Solvatochromic Behaviour

Metal ions sensing, binding and releasing
Metal ions sensing binding and releasing

I. Solution studies

SP-M sol in ACN

20 s UV light

+ Ni$^{2+}$

+ Cd$^{2+}$

+ Co$^{2+}$

+ Cu$^{2+}$

+ Zn$^{2+}$
Metal ions sensing binding and releasing

I. Solution studies

<table>
<thead>
<tr>
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<th>Wavelength (nm)</th>
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<tbody>
<tr>
<td>MC</td>
<td>568</td>
</tr>
<tr>
<td>MC-Ni$^{2+}$</td>
<td>526</td>
</tr>
<tr>
<td>MC-Cd$^{2+}$</td>
<td>507</td>
</tr>
<tr>
<td>MC-Co$^{2+}$</td>
<td>496</td>
</tr>
<tr>
<td>MC-Zn$^{2+}$</td>
<td>478</td>
</tr>
<tr>
<td>MC-Cu$^{2+}$</td>
<td>450</td>
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Metal ions sensing, binding and releasing
Metal ions sensing binding and releasing

II. Capillary coatings
Metal ions sensing binding and releasing

II. Capillary coatings

<table>
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<th>Metal ions</th>
<th>Wavelength (nm)</th>
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<tbody>
<tr>
<td>MC</td>
<td>563</td>
</tr>
<tr>
<td>MC - Ni$^{2+}$</td>
<td>534</td>
</tr>
<tr>
<td>MC - Cd$^{2+}$</td>
<td>522</td>
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<tr>
<td>MC - Co$^{2+}$</td>
<td>508</td>
</tr>
<tr>
<td>MC - Zn$^{2+}$</td>
<td>489</td>
</tr>
<tr>
<td>MC - Cu$^{2+}$</td>
<td>480</td>
</tr>
</tbody>
</table>
Metal ions binding and releasing

![Absorbance vs Wavelength Graph]

- MC - Co$^{2+}$ - MC
- Spiropyran (SP)

508 nm

white light $\downarrow$ + Co$^{2+}$ + UV light
Quantitative binding

Binding capacity: \(~7 \times 10^{-8} \text{ Cu}^{2+} \text{ mole/mm}^3\) coating.
- Self-diagnostic for continuous flow device
- Solvent detection and divalent metal ion detection in micro-capillaries
- Sensing behaviour can be switched on/off remotely using light
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Thank you!