Solvato-morphologically controlled photo-responsive hydrogels for micro-valve applications

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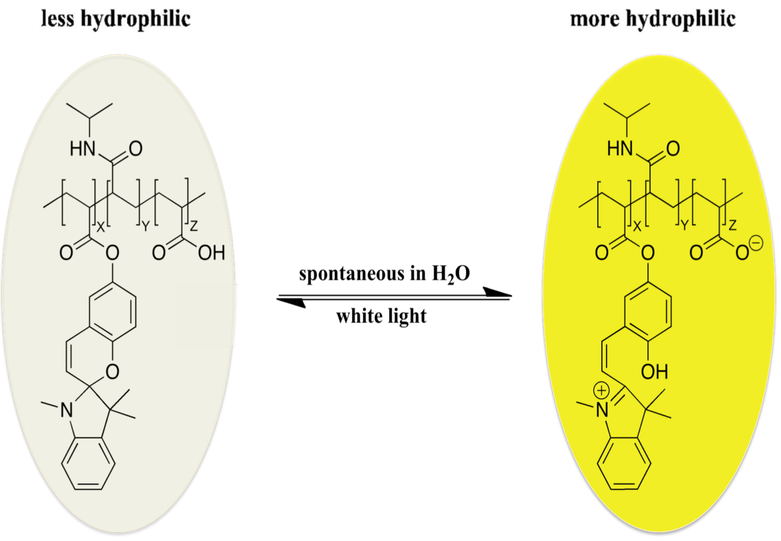
Introduction

Integrating stimuli-responsive materials into microfluidic systems could provide external control over fluid flow and reduce the over-all complexity of the device. In this study photo-actuator hydrogels were generated using a *N*-isopropylacrylamide-co-acrylated spiropyran-co-acrylic acid (p(NIPAAM-*co*-SP-*co*-AA) copolymer. These hydrogels have the ability to contract upon exposure to white light and reswell in the dark. It was shown that the photo-actuation is successfully reversible in a relatively short time period (seconds to minutes). The hydrogels were then incorporated in microfluidic devices as micro-valves for photo-control of flow.

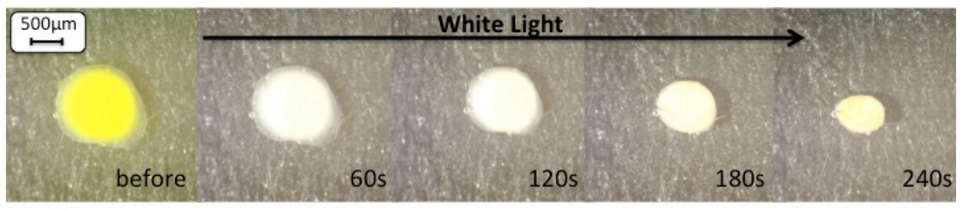
Photo-actuated hydrogels

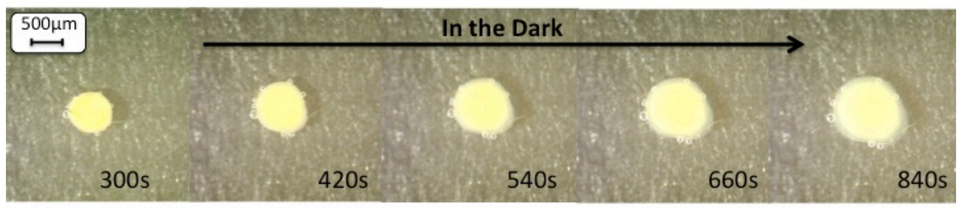
Actuation mechanism



Actuator p(NIPAAm-*co*-SP-*co*-AA) micro-structured hydrogels were photo-polymerised through micro-patterned masks. Their photo-induced shrinking and reswelling mechanism was studied under white light irradiation and in the dark, respectively. In water, the acrylic acid comonomer dissociates, resulting in the protonation of the photochromic spiropyran (SP) to protonated merocyanine (MC-H^+). This form is hydrophilic allowing the hydrogel to swell. Exposure to white light promotes isomerisation of MC-H^+ form to the less hydrophilic SP form, triggering the hydrogel to contract.

Reversible actuation





The hydrogels can reach ~49% of the fully hydrated size after 4 min of white light irradiation. After the removal of the white light the hydrogel re-swelled up to ~91% of the fully hydrated size after 11 min in the dark. This shrinking and re-swelling cycle can be repeated with great reproducibility.

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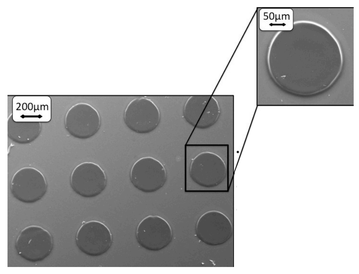
Micro-patterned hydrogels

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

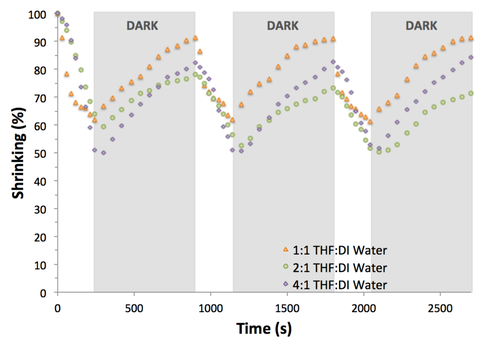


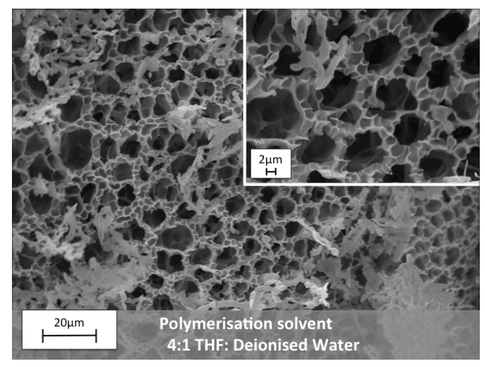
- Circular masks of 1mm diameter.
- Hydrogel height: 60µm.
- Polymerisation time: 10-20 seconds.

Results

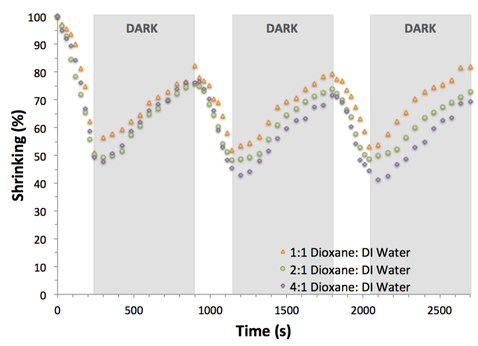
The polymerisation solvent has been shown to directly influence the morphology of the hydrogel, by producing highly porous hydrogels of different pore sizes. This has an impact on the diffusion path length for water molecules moving in/out of the hydrogel, thus enabling the swelling and shrinking kinetics of the hydrogel to be tuned.

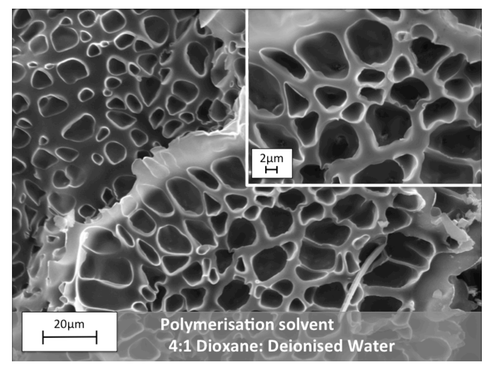
THF : Water mixture





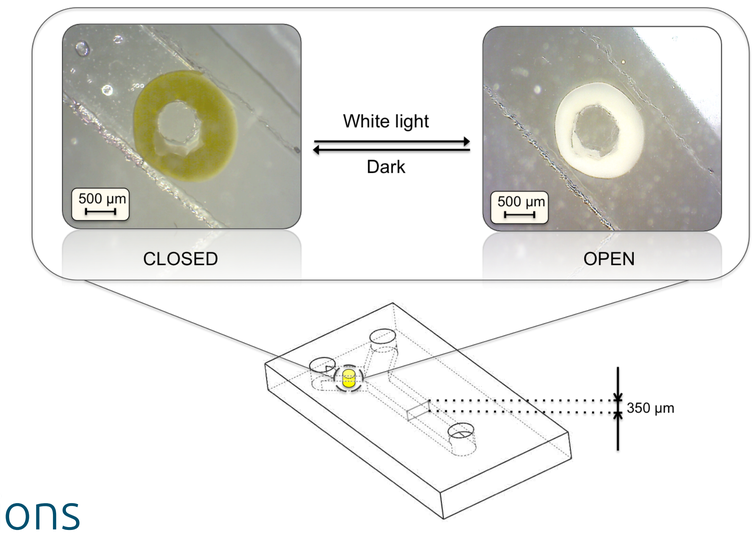
Dioxane : Water mixture





Hydrogel valve application

Hydrogel microstructures were photo-polymerised in-situ inside PDMS/glass microfluidic channels. Exposure to white light causes the valves to contract thus opening the channel, allowing fluid to flow. The opposite was seen when the valve was kept in the dark. These hydrogels can be successfully used as photo-controlled valves in microfluidic systems for repeatable ON/OFF flow modulation in neutral environments.



Conclusions

Integration of photo-responsive hydrogels in microfluidic systems could provide new routes towards the fabrication of smart, externally controlled systems.