Photoresponsive Materials Self-Assembled from Anisotropic Microparticles

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Previous Results …

… Template Assisted Alignment of Colloids…

… Polymeric Network of Microgels…

… and Photoresponsive Polymer Brushes as Glue.

Schürings, Böker et al. Polymers 2016, 8, 413
Focus on the Synthesis of Anisotropic Particles for Self-Assembly…

… by using Microcontact Printing.
Microcontact Printing Approach

- PDMS as Printing Substrate
- Loading of Stamps
- Printing Pressure
- Further Modification

Molecular or Polymeric Inks
Microparticle Monolayer
Particle Release Mechanism
Two Ink Systems

**Polymeric Inks**

Polyethyleneimine and
Poly(methyl vinyl ether-alt-maleic acid)

**Molecular Inks**

Triazolindione (TAD)

TAD click chemistry:

\[
\text{TAD} + \text{Alkene} \rightarrow \text{Alder-ene adduct}
\]
Polymeric Inks: Influence of Ink Thickness on Patch Diameter

Patch Diameter grows with increasing polymer concentration during stamp loading and therefore increasing thickness of ink layer.

Polymeric Inks: Influence of Release Solvent on Patch Geometry

Particle Release in Ethanol

Particle Release in Acetone

2D Patches

3D Patches

PDMS Stamps after Particle Release

Polymeric Inks: Influence of Ink Thickness on Patch Diameter and Thickness

Patch Geometry

Possible Nano Additives
- Quantum Dots
- Magnetic Particles
- Gold Nanoparticle

While release in ethanol leads to 2D patches, the release in acetone produces **3D structures** on the particle. Incorporation of **nano-additives** is possible!

Ink Thickness

1wt% PEI in Acetone

2wt%

3wt%

4wt%

Polymeric Inks: Particle & Patch Size

Ink Thickness

- 1wt%
- 2wt%
- 3wt%
- 4wt%

Particle Size

- 5µm
- 4µm
- 2µm
- 1µm

Sandwich Printing

FITC

FITC / QD

Intaglio Printing using Structured PDMS Stamps: PEI in Ethanol on Silica

Intaglio Sandwich Printing using Structured PDMS Stamps

Transfer to Polymer Particles

Melamineformaldehyde (MF) Microparticles with Polyelectrolyte Inks
Electrostatic Printing with Different Inks

Isoelectric point (IEP) of MF particles at pH ~ 7

- IEP of Poly(methyl vinyl ether-alt-maleic acid): pH < 7
- IEP of Polyethylenimine: pH > 7
Preparation of Bifunctional Patchy Melamine Particles

Fluorescence microscope images of bifunctional patchy particles with patches made of PEI and PMVEMA
Self-Assembly Systems

Electrostatic Coupling

Oppositely charged patches

Amphiphilic Silica-Particles

Alignment induced by Solvent Polarity

Toluene

Water
Self-Assembly Systems

Avidin-Biotin Coupling

Photoresponsive Coupling

Janus Beads by Microcontact Printing with Molecular Ink

= Vinyl SiO₂ microparticles

Glass surface

Polymerization

Pressure

PDMS

TAD ink

2. Stamp

Janus Beads by Microcontact Printing with Molecular Ink

TAD click chemistry:

\[
\text{TAD} + \text{Alkene} \rightarrow \text{Alder-ene adduct}
\]

6.65 µm

TAD initiator

NBD acrylate

AAP acrylate

green fluorescence

Janus Beads by Microcontact Printing

6.65 µm

TAD initiator

NBD acrylate

AAP acrylate

green fluorescence

Scale Bar = 10 µm

Self-Assembly of Janus Beads

\[ \beta\text{-cyclodextrin functionalized } \text{Fe}_3\text{O}_4 \text{ nanoparticles } = \begin{align*} \text{ATRP-TAD} \text{ initiator} & \quad \text{c) 365 nm} \quad \text{d) 520 nm} \\ \text{NBDA} & \quad \text{e) 365 nm} \\ \text{AAPA} & \quad \text{f) 520 nm} \end{align*} 

Scale Bar = 10 µm

Thank you for your attention!

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More information at Posters No. 16 & 23.
Influence of PDMS Treatment with Ethanol

Untreated PDMS

- More oligomers → more hydrophobic → **adhesion to PDMS < cohesion in the ink layer** → Higher density but lower surface charge of patches

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**PEI patchy particles**

<table>
<thead>
<tr>
<th>untreated</th>
<th>treated</th>
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[Images of untreated and treated PEI patchy particles with size indication 2 μm]
PDMS Treatment with Ethanol

Reduced thickness of PEI patches generated by treated PDMS
Stability at different pH Values and Patch Release

pH = 2

pH = 4

pH = 6

pH = 8

pH = 10

pH = 12