Stimuli-Responsive Janus Particles:
Synthesis, Properties, Perspectives Towards Design of Smart Materials

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What are the Janus Particles and their chronicle

“LET ME QUOTE STILL ANOTHER NEW ANIMAL: *THE JANUS GRAINS* …”
DE GENNES, NOBEL PRISE TALK 1991

Their chronicle …

Web of Knowledge

Published Items in Each Year

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2001, Binks
1991, de Gennes
1988, Casagrande & Veyssié

Janus particle
Bicompartmental particle
Dumbbell-like particle
Half raspberry-like particle
Acorn-like particle
Snowman-like particle

What are they good for …

- Electronic paper
- Analytic
- Emulsion stabilizers
- Medicine

...Self-Assembly

http://www2.parc.com/hsl/projects/gyricon/

Particles 2011-Berlin, A. Synytska

S. Granick et. al.
How can they be made …

(i) toposelective surface modification

(ii) dual-supplied spinning disk

(iii) micro fluidics

(iv) Pickering emulsion

(v) biphasic electrified jetting

A. Perro et. al., 2005
S. Granick et. al., 2006-2008
E. Kumacheva et.al., 2006
J. Lahann et. al., 2007
H. Kawaguchi et. al. 2007

etc…
Our Idea & Goal

We want to make them stimuli-responsive

Design of stimuli-responsive bicomponent polymer Janus Particles (JPs) by “grafting from” / “grafting to“ approaches

Particles 2011-Berlin, A. Synytska
Synthesis of Janus particles

A. Synytska, et. al.
Macromolecules 2008, 24, 9669

(highlighted in Science, 2008, 322, 1610)

Particles 2011-Berlin, A. Synytska
Immobilisation of initiator & polymer grafting

„Grafting-From“ Approach via AGET-ATRP

„Grafting-To“ Approach via amide formation

pH, solvent, T, responsive..

Particles 2011-Berlin, A. Synytska

fluorescein acrylate (FoAc)

$\lambda_{\text{ABS}} = 490$ nm (blue)

$\lambda_{\text{EM}} = 514$ nm (green)
Preparation of colloidosomes

Size of colloidosomes: 50 – 200 µm
Preparation of colloidosomes

Colloidosomes size: 20 – 100 µm

APS = 3-Aminopropyl triethoxy silane

striking improvement of quality of SiO2/APS-wax colloidosomes !!

Particles 2011-Berlin, A. Synytska
Preparation of colloidosomes

Unmodified native SiO$_2$ particles

\[ \gamma_{\text{SiO}_2} \approx 72 \text{ mJ/m}^2 \]

SiO$_2$ particles modified with APS

\[ \gamma_{\text{APS}} \approx 49 \text{ mJ/m}^2 \]

\[ \gamma_{\text{WAX}} = 32 \text{ mJ/m}^2 \]

Particles 2011-Berlin, A. Synytska
Immobilisation of initiator

Particles 2011-Berlin, A. Synytska
Poly-(tert butyl acrylate)-JPs

<table>
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<tr>
<th>Sample ID</th>
<th>$M_n$, g/mol</th>
<th>$M_w$, g/mol</th>
<th>PDI</th>
<th>Thickness$^{\text{PDI}}$ (TGA), nm</th>
<th>GD$^{\text{compl. cov}}$, chains/nm$^2$</th>
<th>GD$^{\text{JPs}}$, chains/nm$^2$</th>
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<tr>
<td>PtBA-FoAc</td>
<td>184 000</td>
<td>466 100</td>
<td>2.53</td>
<td>37</td>
<td>0.17</td>
<td>0.68</td>
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Particles 2011-Berlin, A. Synytska

poly-(N-isopropylacrylamide)-JPs

Temperature-responsive and reversible swelling/shrinking of PNIPAAm-JPs

Particles 2011-Berlin, A. Synytska
poly-(N-isopropylacrylamide)-JPs

Temperature-responsive and reversible swelling/shrinking of PNIPAAm-JPs

Particles 2011-Berlin, A. Synytska
Poly-(N-isopropylacrylamide) JPs


Particles 2011-Berlin, A. Synytska
Grafting of second polymer by GT approach

poly (tert butyl acrylate)

poly (2-vinylpyridine)

rhodamine B-based comonomer

$\lambda_{EXC} = 554 \text{ nm (green)}$

$\lambda_{EM} = 580 \text{ nm (red)}$

$M_n = 8450$

$M_w = 33150$

Particles 2011-Berlin, A. Synytska
“Grafting to” of poly-(2-vinylpyridine)

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<th>PDI</th>
<th>GM</th>
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<tr>
<td>P2VP-Rh2</td>
<td>8 450</td>
<td>33 150</td>
<td>3.92</td>
<td>GT</td>
<td>9</td>
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Bi-functional oppositely charged polyelectrolyte - JPs

\[
\text{[H}^+\text{]}\rightarrow \text{[OH}^-\text{]}
\]

Particles 2011-Berlin, A. Synytska
Bi-functional Janus particles: Proof of “Janus Nature”

PtBA-FoAc-JPs  P2VP-Rh2-JPs  PtBA/P2VP-Rh2-JPs

Particles 2011-Berlin, A. Synytska

A. Synytska et. al., Macromolecules 2008 41 (24), 9669–9676
Bi-functional Janus particles: Proof of “Janus Nature”

AFM and SEM images of PtBA-P2VP-JPs and PS-P2VP-JPs

- Sharp border between both grafted polymers (a), (b), (d)
- PtBA has raspberry-structure (a), (c)
- PS yields smooth film on particle surface (d)
- P2VP yields very thin, smooth film on particle surface

Particles 2011-Berlin, A. Synytska
Stimulus-responsive clustering of Janus particles

Regime I: (2<pH<5)
- The JPs form large aggregates.
- PAA (IEP=2.3) is positively and P2VP (IEP=7.5) is negatively charged
→ Large neutralized aggregates are formed due to electrostatic attraction

Stimulus-responsive clustering of Janus particles

Regime I: (2<pH<5)

Regime II: (5.5<pH<7.5)
- Stable dispersion with no coagulation and precipitation.
- P2VP is uncharged and PAA is negatively charged.
- Stability of dispersion mainly determined by ¾ PAA covered surface.

Electrosteric stabilization

Macromolecules 2008, 24, 9669
Stimulus-responsive clustering of Janus particles

Regime I: (2<pH<5)

Regime II: (5.0<pH<7.5)

Regime III: (7.5<pH<9.2)
- Hydrophobic interactions between the P2VP-covered surfaces of the particles lead to the formation of doublets and decrease the stability of the dispersion.

Particles 2011-Berlin, A. Synytska
Application: Design of smart functional coatings.

Idea: using controlled aggregation/clustering of JPs for design of smart materials with desired wetting properties

A. Synytska, et. al. 
Application: modification of textiles with Janus particles

Controlling the pore size, barrier textiles..

A. Synytska, et. al. ACS Appl. Mater. Interfaces 2011, 3, 1216–1220
Wettability of textiles with Janus particles

Particles 2011-Berlin, A. Synytska

Application: Stabilization of emulsions..
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