Cationic-anionic and amphiphilic Janus titania particles for layer-by-layer self-assembly

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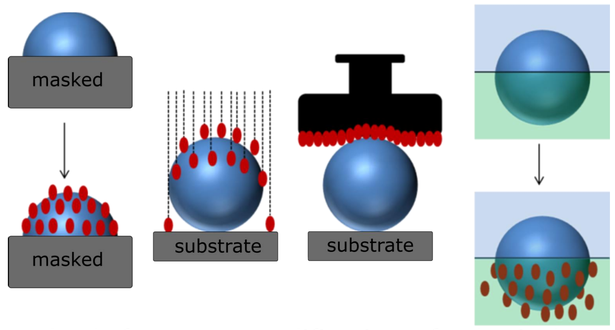
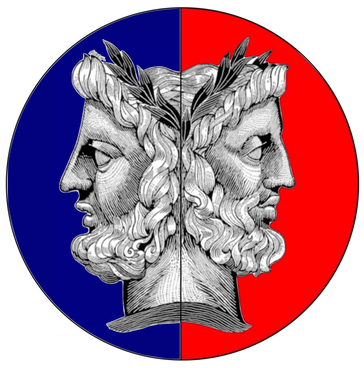
Introduction

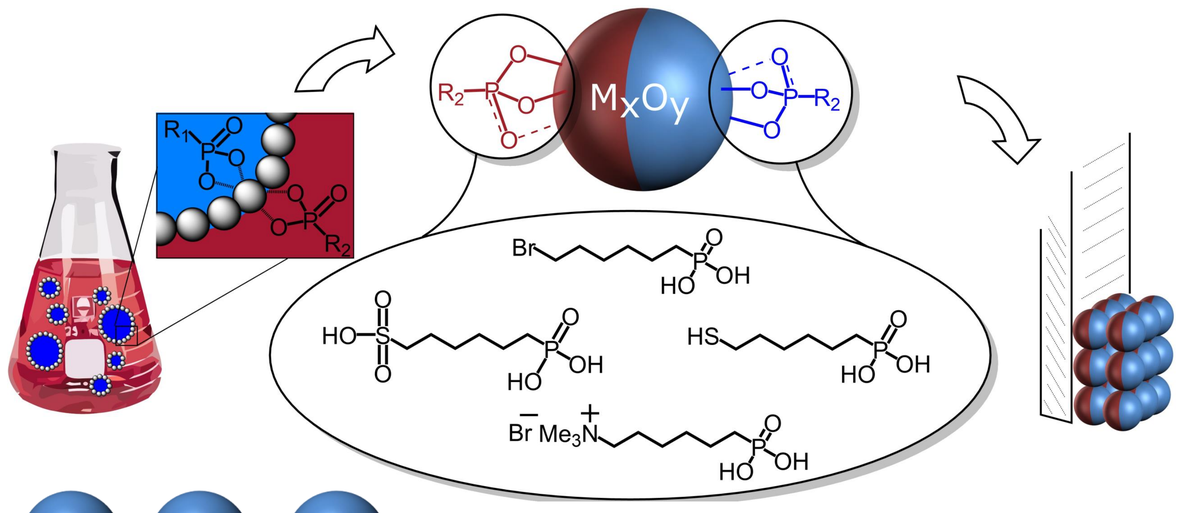
- Janus particles (in reference to the roman god Janus: god of duality) are anisotropic particles whose hemispheres are composed of different materials or differ in their chemical or physical properties.[1,2]
- First introduced by Casagrande *et al.* in 1989.[3]
- Distinction depending on the composition. (organic-organic, inorganic-inorganic, inorganic-organic)
- Strong interfacial activity, self-assembly behaviour, combinations of various opposing properties.
- Varying fields of applications: catalysis, biomedical imaging, non-molecular surfactants, nanomotors, display devices and functional textiles.[1,2]
- Synthesis at interfaces to separate the two hemispheres:

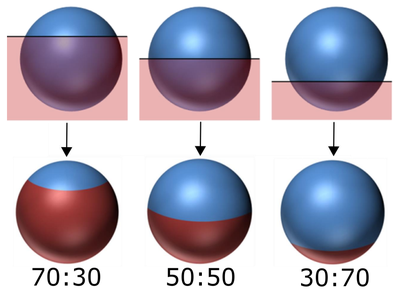


Methods for Janus modification of spherical particles.



Synthetic Concept

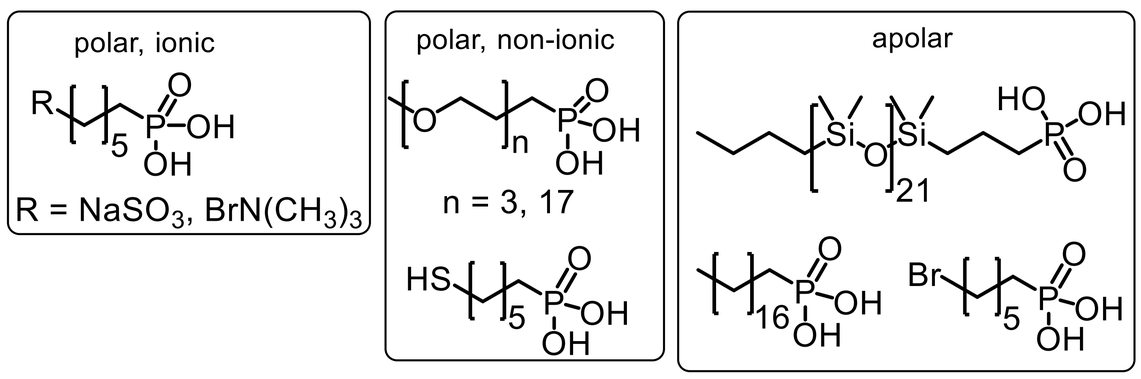




- Concept can be applied to metal and metal oxide particles.
- Janus balance is determined by the wettability of the core particle.

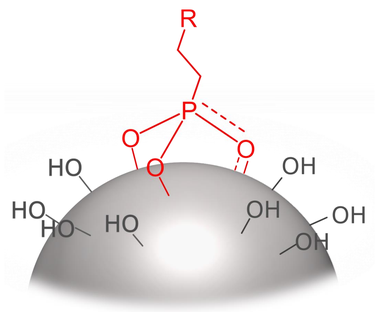
Phosphonic acids

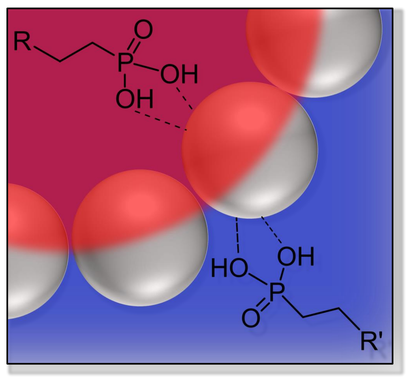
- Various apolar and polar phosphonic acids were synthesised for surface modification of transition metal oxide particles. [4, 6]
- Stable bi- and tridental P-O-M binding to the particle surface.[5]
- Fast reaction rate allows the anisotropic functionalisation in oil-water Pickering emulsions.[4]



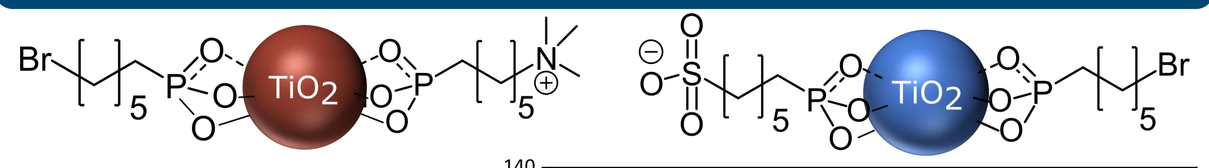
Modification in Pickering emulsions

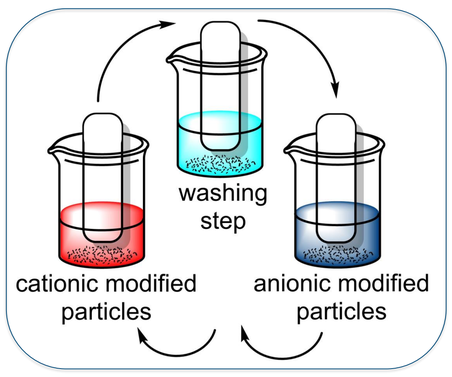
- In Pickering emulsions the emulsified droplets get stabilized by micro- or nanoparticles located at the liquid-liquid boundary.
- A fast modification step (e.g. with phosphonic acids) prevents particle rotation.
- Separation of hydrophilic and hydrophobic reaction compartment allows a differentiating reaction between the surface areas.
- Both particle hemispheres can be modified simultaneously.



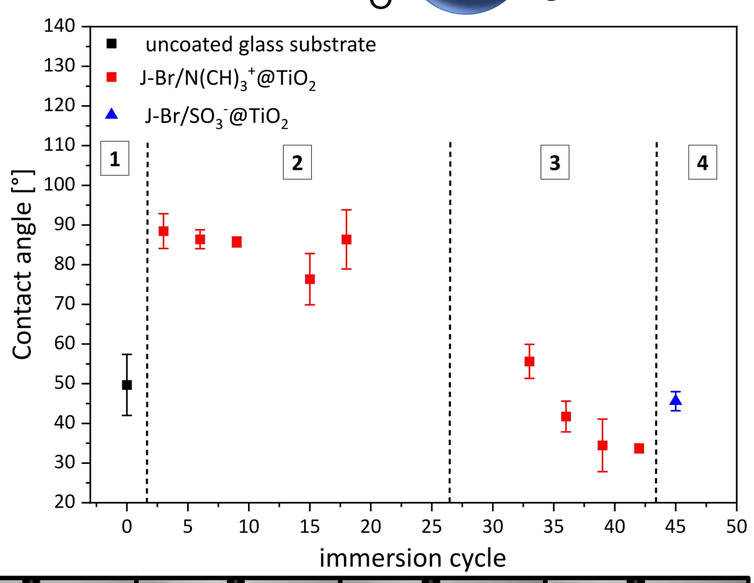


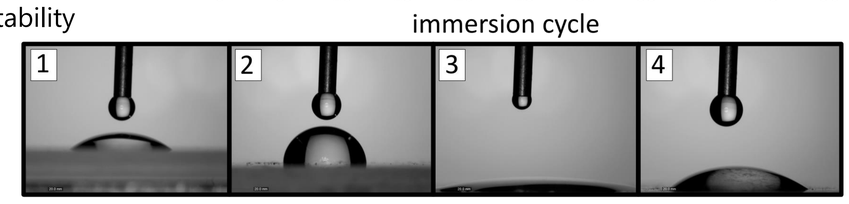
Layer-by-layer deposition





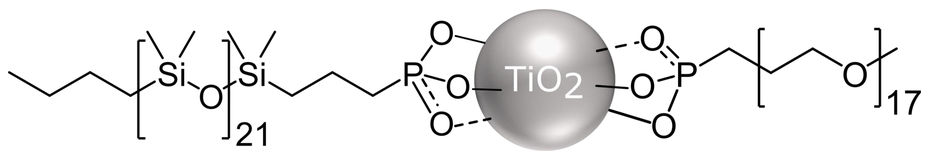
- Layer-by-Layer deposition of ionic-modified Janus particles.
- Changing surface wettability revealed Janus character.





Water contact angle on glass slides depending on the immersion cycle in suspensions of ionic Janus-particles.

Emulsion stabilization

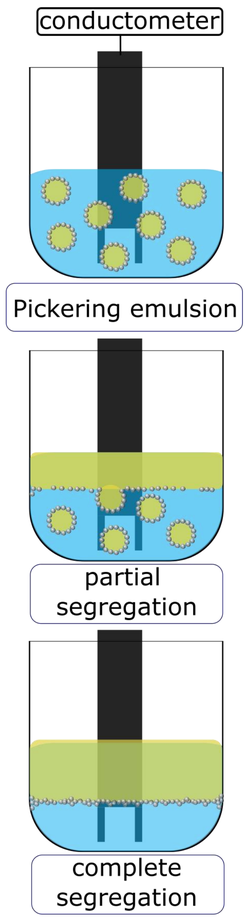


- Amphiphilic Janus particles stabilised toluene-in-water emulsions.
- Time until segregation was determined via conductivity measurements.

➔ Janus particles show strongest emulsion stabilization behaviour compared to isotropic or unmodified particles.

Table 1: Points of 90% phase separation of the toluene-in-water Pickering emulsions containing the modified titania particles.[4]

particles	t [min]
TiO_2	10
PDMS@TiO_2	6
PEG@TiO_2	15
statistic-PEG/PDMS@TiO_2	510
Janus-PEG/PDMS@TiO_2	3028



Conclusion

- Straightforward synthesis of phosphonate surface active agents with functional groups.
- Titania nanoparticles were anisotropically modified in toluene-in-water Pickering emulsions.
- pH-stable charges were attached to particle surfaces.
- Layer-by-layer deposition of nanoparticles on glass substrates.
- Properties of substrate were adjusted by layer-by-layer deposition.
- Amphiphilic Janus particles show surfactant-like behavior.

References

[1] A. Walther and A. H. E. Müller, *Chem. Rev.*, 2013, **113**, 5194–5261.
[2] N. Müller, C. Heinrich, K. Abersfelder and G. Kickelbick, *Chemie in unserer Zeit*, 2016, **50**, 392–399.
[3] C. Casagrande, P. Fabre, E. Raphaël and M. Veyssié, *Epl*, 1989, **9**, 251–255.
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[5] M. Raza, A. Bachinger, N. Zahn and G. Kickelbick, *Materials* 2014, **7**, 2890–2912.
[6] C. Heinrich, L. Niedner, B. Oberhausen and G. Kickelbick, Langmuir, 2019, 35, 11369–11379.