Ionic and amphiphilic Janus metal oxide particles for self-assembly at liquid-liquid and solid-liquid interfaces

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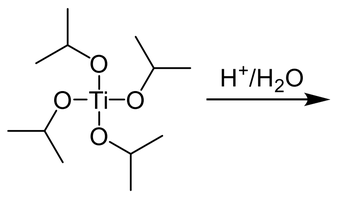
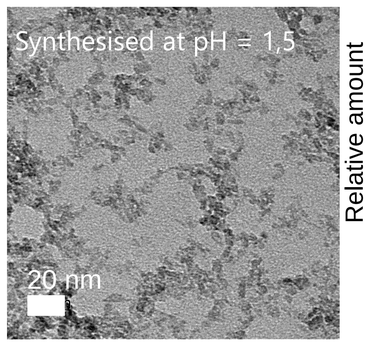
Introduction

- 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]
- The particles can be classified according to their composition (organic-organic, inorganic-inorganic, inorganic-organic)
- Janus particles reveal high interfacial activity and pronounced self-assembly behaviour
- A variety of application exists for Janus particles: catalysis, biomedical imaging, non-molecular surfactants, nanomotors, display devices and functional textiles[1,2]
- The synthesis of these particulate systems must usually occur at interfaces that allow chemical discrimination of the hemispheres

Titania nanoparticles



- Synthesis of surfactant-free titania nanoparticles by an acidic sol-gel process, using either aq. HCl or aq. HNO_3 as acid[4]
- Synthesis at different pH values (1,5 or 2,5) to obtain different particle diameters



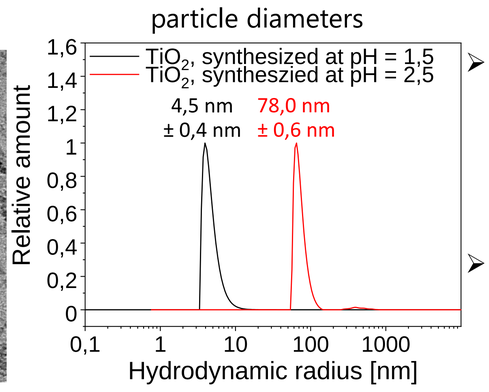


Fig. 2: DLS of as-prepared titania in water.

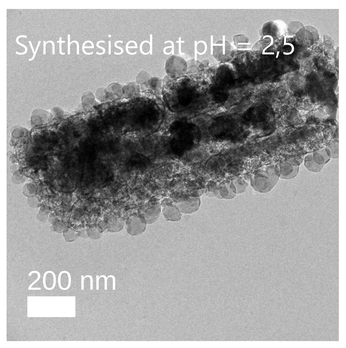


Fig 1: TEM images of titania particles.

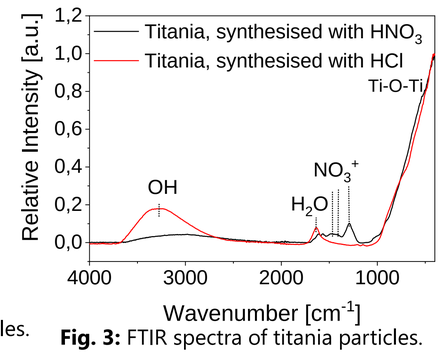


Fig. 3: FTIR spectra of titania particles.

- Small particles build stable dispersions in water, whereby larger particles tend to agglomerate
- PXRD shows mainly the formation of Brookite (50-60 wt%) and Anatase (5–35 wt%) phases
- For particles synthesised at pH 2,5 up to 40 wt% amorphous phase is obtained
- FTIR spectra of titania synthesised using aq. HNO_3 reveals remaining NO_3^+ ions adsorbed to the particles surface

Isotropic ionic modified titania particles

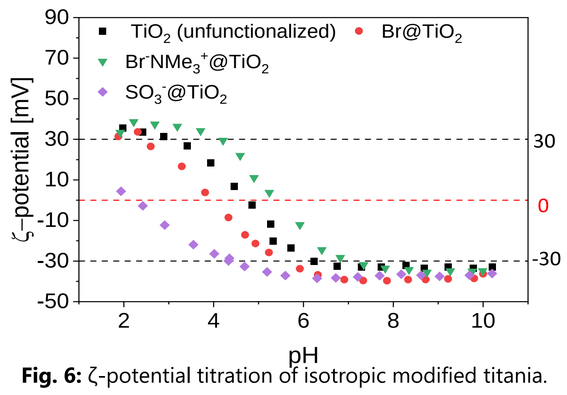


Fig. 6: ζ-potential titration of isotropic modified titania.

Table 2: Isoelectric points of different modified titania particles.

	IEP
TiO_2 (unmodified)	4,75
$N(CH_3)_3^+@TiO_2$	5,41
$SO_3^-@TiO_2$	2,23
$Br@TiO_2$	3,97

- ζ-potential titrations reveal the ionic character of titania modified with $^-Br\ ^+N(CH_3)_3C_6H_{12}PO_3H_2$ and $HSO_3C_6H_{12}PO_3H_2$ over a wide pH range
- To invest their assembly behaviour particles were deposit on various surface-functionalized silicon wafers
- $^-SO_3@TiO_2$ shows poor adsorption on unmodified wafers, whereby it adsorbs homogeneously on cationic modified wafers
- $^+NMe_3@TiO_2$ shows opposing behaviour

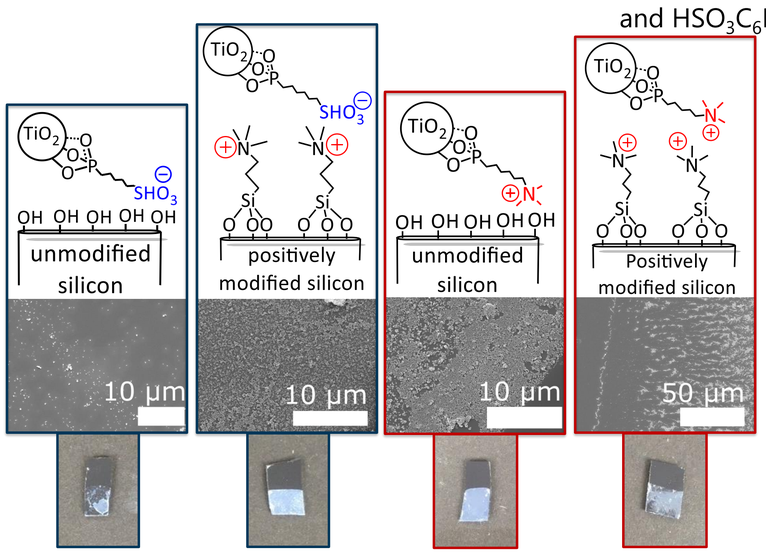
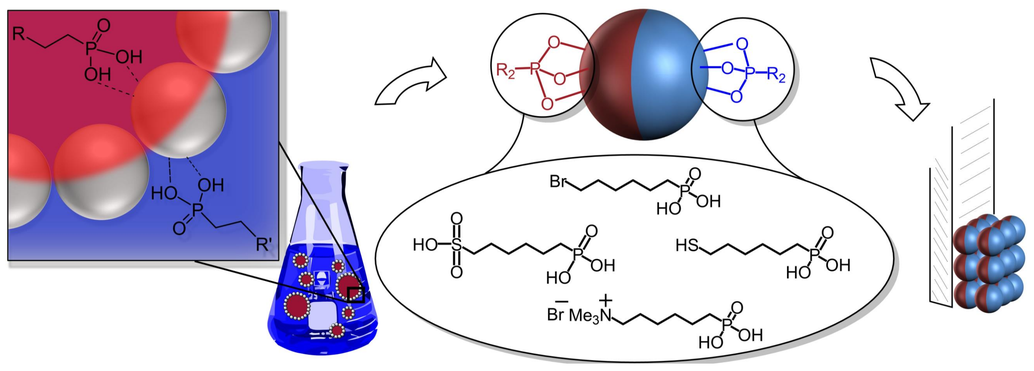


Fig. 7: Deposition of ionic modified titania on various modified silicon wafers.

Conclusion

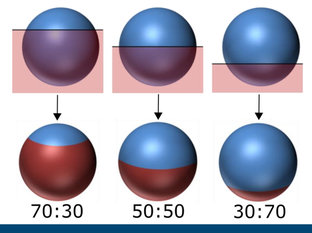
- Synthesis of titania nanoparticles and phosphonic acids with apolar and ionic functional groups
- ζ-Potential titrations show pH stable ionic charges at the particles surface
- The ionic particles were successfully deposit on silicon substrates depending on the modification of the substrate's surface
- Changing wettability of glass substrates after deposition of the particles provide first evidence of their Janus-character

Janus-Modification in Pickering emulsions



- In Pickering emulsions, the emulsified droplets get stabilized by micro- or nanoparticles located at the liquid-liquid boundary
- By choosing coupling agents that bind quickly to the surface, particle rotation is prevented
- Separation of hydrophilic and hydrophobic reaction compartment allows a differentiating reaction between the surface areas
- Both particle hemispheres can be modified simultaneously
- Concept can be applied to metal and metal oxide particles
- Janus balance is determined by the wettability of the core particle

Various Janus balances:



Phosphonic acids as surfactants

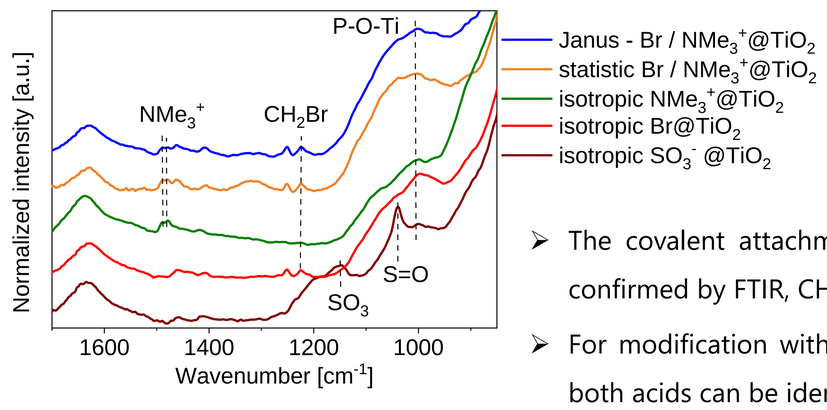


Fig. 4: FTIR spectra of modified titania.

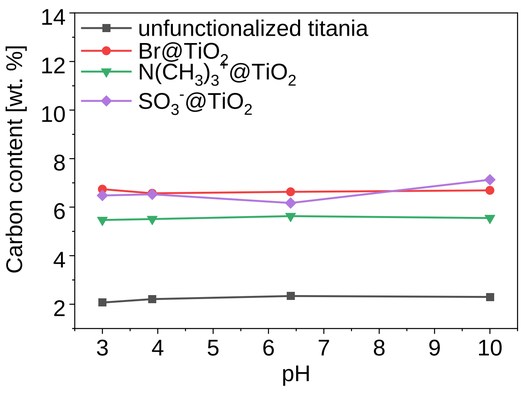
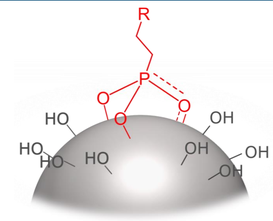


Fig. 5: C content after different pH treatments.

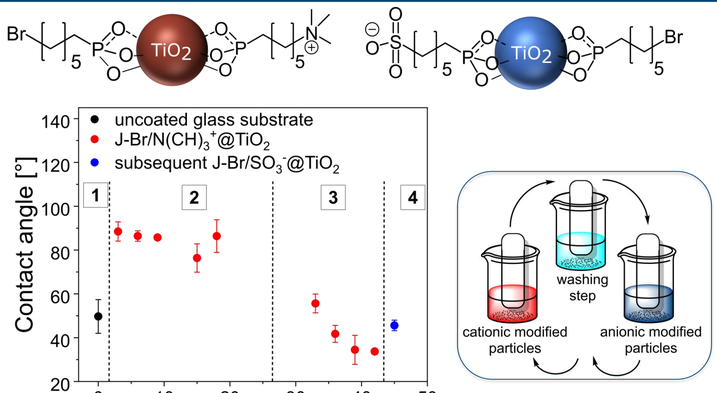


- The covalent attachment of the phosphonic acids is confirmed by FTIR, CHN, and solid-state NMR
- For modification with two different phosphonic acids both acids can be identified by FTIR
- CHN after treatment of the particles with NaOH and HCl at various pH values demonstrates a stable attachment over a wide pH range

Table 1: Amount of phosphonic acid at the particles surface in mmol*g^{-1} for isotropic modified particles by TGA and CHN.

	5 nm	78 nm
$N(CH_3)_3^+@TiO_2$	0,4	0,8
$SO_3^-@TiO_2$	0,4	0,7
$Br@TiO_2$	1,2	1,2

Janus evidence by switching contact angle



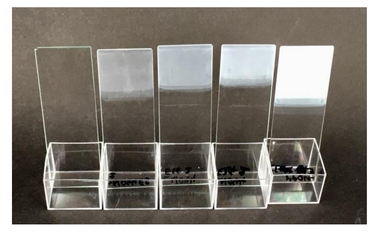


Fig. 8: Alternated deposition of $NMe_3^+@TiO_2$ and $^-SO_3@TiO_2$ on glas substrates as model system.[6]

Fig. 9: Water contact angle on glass slides depending on the immersion cycle in suspensions of ionic Janus-particles.

- Layer-by-Layer deposition of ionic-apolar modified Janus particles on glass substrates
- Changing surface wettability from apolar to polar after 30 dipping cycles demonstrates the Janus character

References

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[2] N. Müller, C. Heinrich, K. Abersfelder and G. Kickelbick, *Chem unserer Zeit*, 2016, **50**, 392–399.
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[4] M. Raza, A. Bachinger, N. Zahn and G. Kickelbick, *Materials,* 2014, **7**, 2890–2912.
[5] N. Zahn and G. Kickelbick, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2014, **461**, 142–150.
[6] C. Heinrich, L. Niedner, B. Oberhausen and G. Kickelbick, *Langmuir*, 2019, 35, 11369–11379.