Kaolinite-Based Janus Particles

Large-Scale, Low-Cost Fabrication of Janus-Type Emulsifiers by Selective Decoration of Natural Kaolinite Platelets**

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Bifunctional and/or anisometric Janus^[1] particles have proven to be superior to spherical and chemically isotropic colloids for a wide range of promising applications, such as in nanorobots,^[2] physical sensors,^[3] microrheology,^[4] drug delivery,^[5] magnetic storage,^[6] electronic devices,^[7] surfactants, and compatibilizers.^[8] Nevertheless, large-scale technical applications have been halted by the restricted accessibility of these polar colloids. Established synthesis methods that allow for breaking the symmetry are laborious and expensive.^[9-11] Previously, microphase separation of triblock terpolymers,^[12] the arrangement of symmetrical colloids at an interface followed by modification of the exposed hemisphere by microcontact printing,^[9] and different masking techniques^[13,14] have been used. However, nature provides multifunctional spherical nanoparticles, such as proteins. Specific modifications at different functional sites of ferritin or transthyretin have been reported.[15,16] Recently, Kotov et al.^[17,18] pointed out that semiconductor nanoparticles may resemble such proteins inasmuch as the specific local packing into truncated tetrahedrally shaped morphologies leads to breakage of symmetry of these nanoparticles, which may in turn trigger self-assembling of these nanoparticles on the mesoscale by directional attraction that is mainly of electrostatic nature. Symmetry-breaking in solids and minerals is, however, not limited to the mesoscale. Crystal structures that are inherently polar at the atomistic level are frequently encountered.^[19] As a consequence of the polar crystal structure, opposing crystal faces carry different functional groups.

Herein, we show that the natural mineral kaolinite [Al₂Si₂O₅(OH)₄], an abundant, ubiquitous, and inexpensive (€200/tonne) mineral, possesses Janus character. Kaolinite is found as anisometric platelets with large aspect ratios that are typically in the range of 20:1-40:1. Consequently, polar basal planes dominate the external surface area.

Kaolinite is a dioctahedral layered silicate (Figure 1 a).^[20] The octahedral layer and tetrahedral layer are linked to a 1:1 lamella with the basal surfaces confined by differing functional groups (Figure 1 b,c). The lamellae are stacked in a polar mode through strong hydrogen bonds (Figure 1a). Furthermore, as no twinning has usually been observed,^[21] the two opposing external basal planes of the kaolinite platelets consist of an Al₂(OH)₄ octahedral layer (octahedral surface, OS), which is capped by μ -hydroxy groups at the external surface, and the other side is capped by a SiO4 tetrahedral layer (tetrahedral surface, TS). Although even pristine kaolinite displays a Janus character, the surface tension of the two unmodified external basal surfaces is similar. Although the idealized chemical formula would suggest natural kaolinite to be charge-neutral, it nevertheless possesses a small cation-exchange capacity (CEC) owing to an isomorphous substitution in the tetrahedral layers, which can

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[**] ₩ €+	/e thank the German Science Foundation (SFB 840) and the Elite	
tic O M Jü	onal Graduate School "Structure, Reactivity and Properties of Dxide Materials" within the Elite Network Bavaria and Bayer Material Science for financial support. The authors thank Prof. Dr. Grgen Senker for providing the NMR equipment.	Figure 1. a) Crystal structure of kaolinite viewed perpendicular to the stacking direction (c^*), which shows the polar nature of each individ ual 1:1 lamella and also of their stacking. b) Top view of the external tetrahedral surface (TS), which is confined by basal oxygen atoms
	upporting information for this article is available on the W/W/W	from the tetrahedral layer c) Top view of the external octahedral

under http://dx.doi.org/10.1002/anie.201106710.

only be counterbalanced at the outer TS by hydrated cations^[22] that render the surface hydrophilic. The OS is capped by hydrophilic μ -Al₂-OH groups. Consequently, the Janus character inherent to the kaolinite structure is ineffective without selective modification of the external surfaces that amplifies the difference in chemical nature of the opposing basal surfaces (depicted in Figure 2). We used a



Figure 2. Amplification and fine-tuning of the Janus character: Selective modification of the TS and OS of kaolinite by covalent grafting with catechol and cation exchange with $[Ru(bpy)_3]^{2+}$, respectively. The molecular structures of modifiers are shown in the gray box.

natural coarse-grained kaolinite with typical dimensions of the ideally hexagonal platelets that were 2 μ m in diameter and 70 nm in height (Supporting Information, Figure S1). The specific surface area was approximately 4 m²g⁻¹, and about 90% of this area could be attributed to the external basal surfaces. Nevertheless, the detection of monolayer coverage of the external surfaces required highly sensitive analytical methods, and the proof of the selective modification is inherently difficult.

Selective modification of the TS was achieved by simple ion exchange^[23] of the hydrated inorganic counterions (typically Na⁺) by organic or metal-organic cations that render this surface more hydrophobic. For analytical reasons, we selected the $[Ru(bpy)_3]^{2+}$ complex (bpy=2,2'-bipyridine), which is known to exhibit a high selectivity for clay surfaces and for which emission properties adsorbed onto clays have been intensively studied.^[24] Successful cation exchange can even be followed visually, as the color of the modified kaolinite changes from white (pristine) to orange (modified). The adsorption isotherm of $[Ru(bpy)_3]^{2+}$ was monitored by UV/Vis spectroscopy (Supporting Information, Figure S2). The observed adsorption capacity (2.6 mval/100 g) corresponded with the CEC of the pristine kaolinite sample, which was determined using the Ba²⁺ method ((2.7 ± 0.1) mval/ 100 g).^[25]

Whereas changing the surface tension of one external surface already boosts the Janus character of kaolinite, additional selective modification of the second external surface is highly desirable for fine-tuning the Janus character. Modification of the OS is, however, more difficult. Recently, we showed that μ -Al₂-OH groups could be covalently grafted by glycol,^[26] demonstrating sufficient reactivity of the OS. Catechols are known to form strong inner-sphere surface complexes with titania surfaces that are chemically similar to the OS of kaolinite.^[27,28] These siderophiles are expected to have a pronounced chemical affinity for the aluminol groups of kaolinite. For analytical reasons, we selected a P-labeled catechol, which allows for the detection of immobilization by ³¹P-MAS (magic-angle spinning) solid-state NMR spectroscopy. The spectra from pristine kaolinite (Supporting Information, Figure S3a) has one sharp ³¹P signal at -4.23 ppm, which may be assigned to a well-known accessory phosphate mineral called gorceixite [BaAl₃(PO₄)₂(OH)₆].^[29] This trace impurity (P content ca. 0.12% by weight) cannot be selectively removed by physical or chemical treatment. EDX (energy-dispersive X-ray spectroscopy) element mapping of phosphorus and barium showed that the impurity phase is well-separated from the kaolinite particles and that the basal surfaces were completely free from any phosphorus and barium impurities (Supporting Information, Figure S4).

The ³¹P spectrum of modified kaolinite (Supporting Information, Figure S3b) featured a signal at 34.0 ppm in addition to the gorceixite signal at -4.2 ppm. The signal at 34.0 ppm is due to the phosphorus linker from the catechol that was immobilized on the kaolinite. Neither the peak position nor the intensity (normalized) of the ³¹P signal at 34.0 ppm (Supporting Information, Figure S3c) were affected by subsequent modification of the TS by cation exchange, which suggests that catechol immobilization and cation exchange are independent from each other and most likely occur on different surfaces. The chemical environment of the phosphorus in the crystalline impurity is more rigorously defined compared to the linker immobilized on the surface. Consequently, the ³¹P signal of the linker is broader than that of the impurity.

Luckily, the phosphorus-containing impurity may be used as an internal phosphorus standard, which allowed the determination of the minute adsorption capacity of catechol. This adsorption capacity could not be determined by other methods because of the small surface-to-volume ratio of the kaolinite particles.

A comparison of the integral of the ³¹P signal of catechol and that of the trace impurity (Supporting Information, Figure S3b) yields the additional phosphorus content that was introduced by catechol adsorption, which was approximately 0.03 % by weight and corresponded to 1 mval/100 g (details of the calculations are provided in the Supporting Information). Assuming a uniform hexagonal morphology for the kaolinite platelets (thickness 70 nm, diameter 2 μ m), we calculated a reasonably high grafting density of approximately one linker per two unit cells (92 Å²). Furthermore, the edges of the kaolinite platelets expose hydroxy groups that are expected to adsorb catechol as well. Because of the high aspect ratio of the platelets, the specific surface area of the edges was estimated

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to be less than 16% of the OS; therefore, the adsorption capacity of the edges may be neglected.

Although the orthogonality of the adsorption of catechol and $[Ru(bpy)_3]^{2+}$ already suggested a selective adsorption of the two modifiers at distinct surface sites, unequivocal evidence for the selectivity requires a sensitive analytical method with sufficient spatial resolution.

ToF-SIMS (time-of-flight secondary-ion mass spectrometry) combines high surface sensitivity with sufficient lateral resolution ($< 1 \mu m$), thus allowing individual platelets deposited from dilute suspensions onto an appropriate substrate to be analyzed. The high aspect ratio ensures a textured sedimentation from suspensions with the basal planes orientated parallel to the substrate. We used two different substrates: silicon wafers and gold-coated silicon wafers. As it turned out, the drop-casted kaolinite platelets showed different orientations on the different substrates. In addition, the modifiers for the TS and OS yield distinctly different secondary-ion fragments. Furthermore, the exposure time to the primary ion beam (analysis time) was chosen so that not only secondary ions from the modifiers were detected but also secondary ions from the underlying surfaces. In total, we estimated that 1-2 nm of material were removed during the analysis; as this is much less than the typical thickness of the kaolinite particles, we can be sure that the acquired data refer solely to the exposed surfaces.

Secondary-ion images were acquired by rastering the ion beam multiple times over a selected area and recording (at high sensitivity but low mass resolution) a full mass spectrum at every pixel. In Figure 3, only selected masses that correspond to atomic or molecular secondary ion fragments characteristic for the fragmentation of the OS and TS modifiers are shown in the cumulative images. The low mass resolution means that there are unresolved mass interferences; for example, there is another secondary ion present at m/z = 102 in addition to Ru⁺.

On both substrates, the kaolinite platelets can be easily located by the silhouettes that become apparent in the secondary ion images of Au^+ and Si^+ . The location of the platelets was further confirmed by the high intensities of the silicon and aluminim masses, which are the main constituents of kaolinite (Supporting Information, Figures S5 and S6).

We selected the characteristic mass image of the modifiers of the TS (Ru⁺, Figure 3b) and of the OS (P⁺, Figure 3c and $C_3H_5O_2^+$, Figure 3d; additional masses are shown in the Supporting Information, Figures S5 and S6). On the goldcoated substrate (Figure 3 A b), the intensity of the Ru⁺ mass on the kaolinite particles was below the level of significance, and the intensity of the Ru⁺ mass recorded in the background of the substrate was greater than that recorded on the kaolinite particles (unresolved mass interference). However, the intensities of the fragments related to the phosphorus linker (P⁺, Figure 3Ac and $C_3H_5O_2^+$, Figure 3Ad) were significantly greater on the kaolinite platelets compared to the background. For unknown reasons, the intensities of these two masses appeared patchy, which was most likely due to the inhomogeneous reactivity of the OS towards catechol because the more reactive sites (kinks) adsorbed more of the modifier. On the gold-coated substrate, the TS of the kaolinite platelets



Figure 3. Mass fractions determined using SIMS measurements on A) a gold-coated silicon wafer (200 μ m × 200 μ m) and B) on a silicon wafer (100 μ m × 100 μ m). Secondary-ion images of: a) Au⁺ (m/z=197; (A)) Si⁺ (m/z=28; (B); wafer material), b) Ru⁺ (m/z=102) (TS modification), c) P⁺ (m/z=31) (OS-modification), and d) C₃H₅O₂⁺ (m/z=73) (OS modification). Both scale bars for relative intensity of the masses (right-hand side: black=low intensity, white=high intensity) and size (d) refer to the complete set of four masses measured on each substrate.

was oriented towards the wafer; the OS was exposed to the analysis chamber and was selectively modified by the phosphorus-labeled catechol.

The mass images were different on the silicon substrate (Figure 3B) compared to those on the gold-coated substrate. At the positions where the particles were located, the mass signal that was due to the phosporus-labeled catechol was below the detection limit, while a high intensity was observed for the mass signal from Ru^+ . This result suggests that the kaolinite platelets were facing the ion beam with the TS, and that the TS was selectively modified by $[Ru(bpy)_3]^{2+}$.

The arrangement of the kaolinite particles on the substrate was defined and not random. A comparison of the sediments on the gold-coated and silicon wafers in Figure 3 indicates that either the catechol (P-labeled) or $[Ru(bpy)_3]^{2+}$ was detectable. This result demonstrates not only that a selective modification of kaolinite platelets is feasible, but that, surprisingly, a selective alignment on one specific basal plane was achieved.

We hypothesize that for selective orientation, the platelets must be far enough away from the surface of the substrate to allow for rotation $(>2 \,\mu m)$ and that the specific interaction with the substrate must therefore be long-range, which suggests that electrostatics likely play a major role. Although the zeta potential of the platelets was diminished after cation exchange with $[Ru(bpy)_3]^{2+}$, the surface potential of the TS remained negative (-36 mV and -18 mV for pristine and $[Ru(bpy)_3]^{2+}$ -exchanged kaolinite, respectively). The surface potential of the gold-coated wafer was expected to be positive at pH 5 because of oxidation during the cleaning procedure.^[30] In contrast, the surface potential of the silicon wafer was negative.^[31] If electrostatics does induce a selective orientation, the negatively charged TS should be pushed away from the silicon substrate and attracted to the goldcoated substrate, which is in agreement with experimental observations (Figure 3).

As a preliminary test to demonstrate the superiority of the Janus-type particles as Pickering emulsifiers, we investigated their potential as stabilizers for oil-in-water emulsions. For this particular emulsion, one of the external basal surfaces of kaolinite must remain hydrophilic, and therefore only the TS was rendered more hydrophobic while the OS was left unchanged and hydrophilic. Exchanging the hydrophilic inorganic cations at the TS with hydrophobic hexylammonium ions ensured a good wettability of the modified TS with the hydrophobic oil phase. For comparison, emulsions were prepared with pristine and TS-modified kaolinite, respectively (Figure 4). The pristine kaolinite reflected the stabilization of the emulsions through a simple Pickering effect. The emulsions prepared with the pristine kaolinite quickly coalesced, and oil droplets with sizes in the range of millimetres were observed after 48 h. Some of the kaolinite

Figure 4. Oil-in-water emulsions stabilized with pristine kaolinite (left) and hexylammonium-modified kaolinite (right) after 48 h.

formed sediment on the bottom of the vessel. However, the emulsions with the TS-modified kaolinite were stable for months and yielded smaller droplet sizes. Typical droplet sizes achieved with the modified kaolinite were in the range of $100 \,\mu m$ (Supporting Information, Figure S7).

The emulsifying power of the modified particles indicated a high affinity of assembly at the oil–water interface. This indirectly confirmed the selective nature of the modification because platelets that were concomitantly modified at the TS and OS sites were expected to be tracked into the oil phase because of the purely organophilic nature of both the OS and TS sites of dually modified platelets.

In summary, we have presented evidence for the Janus character of inexpensive natural kaolinite platelets. Unfortunately, the TS and OS sites of pristine kaolinite were hydrophilic, and the Janus character was hidden. Fortunately, the selective modification of the TS and OS was feasible, and the modification was achieved by cation exchange and covalent grafting of catechol ligands, respectively. The modification is not limited to the model reactions selected for the proof-of-concept experiments performed herein; rather, a wide range of selective modifications are possible and will allow the chemical nature of the Janus surfaces to be fine-tuned. Moreover, the Janus character was emphasized by the plate morphology and large aspect ratio. Because of the facile modification, the environmentally benign nature of kaolinite and its low-cost availability, the range of possible applications is limitless. From an industrial point of view, the unique surface activity of Janus particles that arise from the combination of the Pickering effect and the amphiphilic nature of the Janus particles holds the largest potential, such as for strong emulsifiers that control the microstructure of polymer blends.

Received: September 21, 2011 Published online: December 27, 2011

Keywords: emulsions · kaolinite · organicinorganic hybrid materials · polar platelets

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