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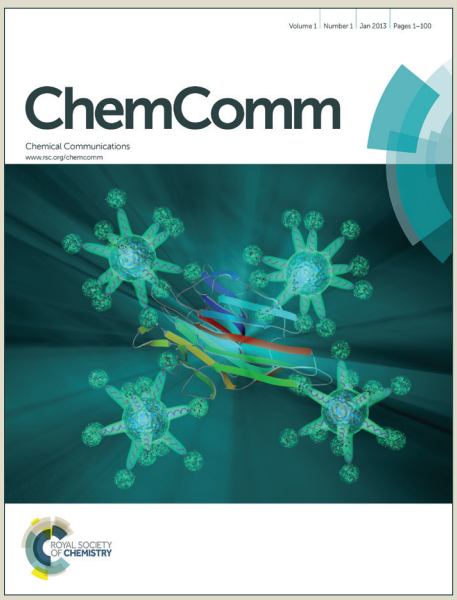

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ARTICLE TYPE

Ionic Liquid Functionalized Janus Nanosheets

Xuyang Ji[a,b], Qian Zhang [b], Fuxin Liang[a], Qinan Chen [b], Xiaozhong Qu[a], Chengliang Zhang[a], Qian Wang[a], Jiaoli Li[a], Ximing Song*[b] and Zhenzhong Yang*[a]

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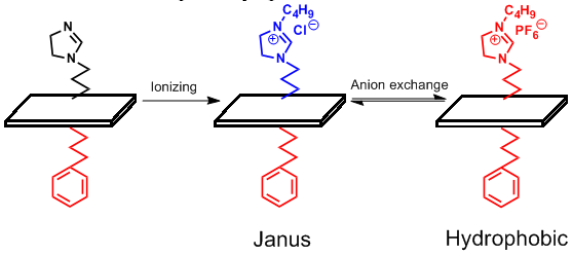
Ionic Liquid functionalized Janus nanosheets are synthesized by selective treatment of the imidazolin terminated side of Janus nanosheets while the other side is preserved. Janus performance of the nanosheets thus emulsion stability is reversibly triggered by anion exchanging.

Janus materials with two compositions distinctly compartmentalized onto the same object, have received increasing attention.[1-5] Among their diversified performances,[6-13] they are amphiphilic and thus can serve as solid surfactants. Shape and composition of Janus materials play significant roles in their performance. Janus nanosheets are more difficult to turn over at an emulsion interface due to their highly anisotropic shape, and make an emulsion more stable than their Janus spherical counterparts.[14-17] Composition of Janus materials determines their functions and potential applications. For example, magnetic Janus nanocomposites can manipulate cells upon attachment under a magnetic field.[18] We have reported thermal or pH responsive Janus composite nanosheets by favourable grafting polymer chains onto one side of Janus inorganic nanosheets,[17] Janus reversion of the nanosheets is thus triggered accordingly.[19-20] It will be attractive if the Janus nanosheets are responsive to ions, stability of the emulsion can be simply manipulated by adding salts. Ionic liquids (ILs) can meet the requirement.[21] As an example, imidazole based ionic liquids can experience reversible hydrophobic-hydrophilic transition by anion exchanging.[22-23] It is expected that once Janus reversion will be achieved thereby if one side is functionalized with the ionic liquids. Besides, functional materials are easier to grow within the ionic liquids by specific interactions.[24-29]



Scheme 1. Synthesis of ionic liquid functionalized Janus silica nanosheets and anion triggered Janus-hydrophobic reversion. Hydrophilic imidazolin and hydrophobic groups are terminated onto the corresponding sides of the parent Janus nanosheets. The imidazolin terminated side is functionalized with an ionic liquid after ionizing with 1-chlorobutane, while the other hydrophobic side is not influenced. Hydrophilic performance of the side (blue) becomes hydrophobic (red) after anion exchanging. The transformation is reversible by another anion exchanging.

Herein, we report synthesis of ionic liquid (IL) functionalized Janus nanosheets (Scheme 1). Along the route towards Janus hollow spheres,[8] an example silane containing triethoxy-3-(2-imidazolin-1-yl) propyl- group is used instead of amine- group contained silane, forming Janus hollow spheres with 2-imidazolin-1-yl group terminated onto the exterior surface, while the interior surface is terminated with phenyl- group. The corresponding imidazolin based Janus nanosheets are derived by crushing the Janus hollow spheres. The IL based Janus nanosheets are achieved by selective modifying the 2-imidazolin-1-yl group with 1-chlorobutane, while the other hydrophobic phenyl- side is preserved. The hydrophilic side of the Janus nanosheets will transform to be hydrophobic after anion exchanging from Cl^- with PF_6^-. The Janus nanosheets thus become hydrophobic. In reversion, the hydrophobic nanosheets will transform to be Janus after another anion exchanging.

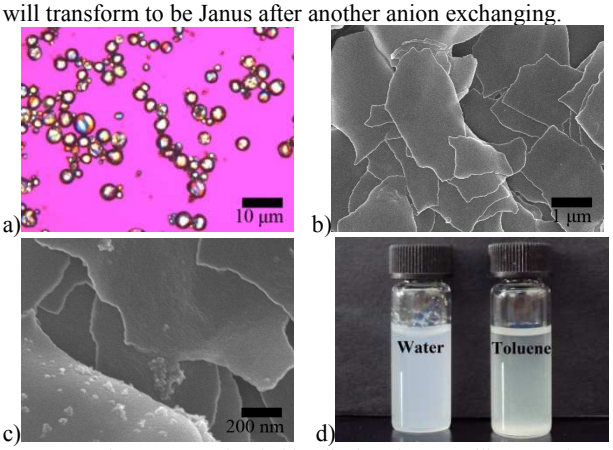


Figure 1. The representative imidazolin based Janus silica nanosheets. a) Polarizing optical microscopy image of the core/shell particle; b, c) SEM images of the imidazolin based Janus nanosheets before and after selective labeling with trisodium citrate capped Fe_3O_4 nanoparticles onto the imidazolin side; d) dispersions of the Janus nanosheets in water (left) and in toluene (right).

In an example aqueous emulsion stabilized with a hydrolyzed styrene-maleic anhydride,[8] the dispersed oil phase is composed of paraffin as a solvent and tetraethoxysilane, triethoxy-3-(2-imidazolin-1-yl) propylsilane and phenyl-triethoxysilane. At a low level of pH for example 3.0 and high temperature above the paraffin melt temperature for example 70 °C, acid catalyzed self-organized sol-gel process occurs at the emulsion interface, forming a silica composite shell. A core/shell particle forms eventually (Fig. S1a). The core paraffin is evidenced by polarizing optical microscopy image (Fig. 1a). After dissolution

of the core, a silica based hollow sphere is derived (Fig. S1b). The exterior surface of the shell should be terminated with the imidazolin group, while the interior surface is the phenyl group. Imidazolin based Janus nanosheets are achieved after crushing the parent Janus hollow sphere by colloid milling. Two sides of the Janus nanosheets are smooth (Fig. 1b). A representative Janus nanosheet about 65±2 nm thick is used as the example (Fig. S2). In order to confirm distinct compartmentalization of the imidazolin group exclusively onto one side, negatively charged trisodium citrate capped Fe_3O_4 nanoparticles are used to label the imidazolin side by a specific interaction. As a result, the imidazolin side becomes coarsening, while the other side remains smooth (Fig. 1c). The nanosheets are well dispersible both in oil and water (Fig. 1d), revealing Janus performance.

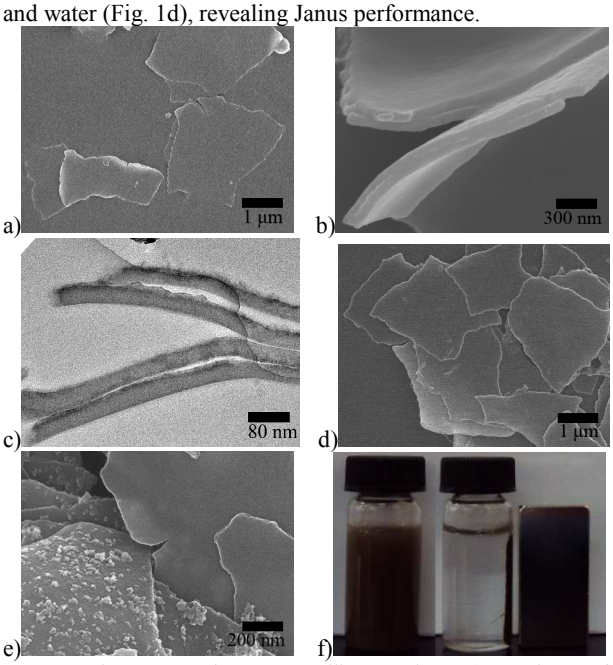


Figure 2. The representative IL-Janus silica nanosheets. a) SEM image of the Cl^- based IL-Janus nanosheet powder after naturally drying the aqueous dispersion; b) SEM image of the Cl^- based IL-Janus nanosheet powder after cryo-drying the aqueous dispersion; c) cross-section TEM image of the nanosheet powder embedded in PMMA; d) SEM images of the Cl^- based IL-Janus nanosheets which are dried from the ethanol; e) SEM image of the IL-Janus Fe_3O_4 composite nanosheets, and f) the dispersion in water (left) and collected with a magnet (right).

After a selective reaction with alkyl halide such as 1-chlorobutane, the imidazolin side becomes ionic liquid functionalized, while the other phenyl- side preserves the hydrophobic. The white powder becomes yellow after this ionic liquid functionalization. Both sides remain smooth. Zeta potential of the IL based Janus nanosheets is +38.1 mV at pH=7.0 (Fig. S3). In comparison, Zeta potential of the imidazolin based Janus nanosheets is +17.2 mV since pKa (7.2~7.4) of imidazolin is slightly above 7.0. Reaction extent is determined by surface element analysis (Fig. S4). The N1s peak at 409.9 eV is assigned to imidazolin, which is about 3%. Cl element is 0.9 % after the ionic liquid functionalization. The IL based Janus nanosheets remain well dispersed both in water and oil due to their amphiphilic performance (Fig. S5). In selective solvents for example water, the Janus nanosheets should be back-to-back aggregated but dispersible with the hydrophilic sides exposed to the aqueous continuous phase. After naturally drying the aqueous dispersion, a kind of bi-layered superstructure is observed (Fig. 2a). In order to freeze the aggregation structure in the dispersion, cryo-drying of the dilute dispersion is employed. As shown in Figure 2b, the Janus nanosheets form the 1:1 back-to-back aggregation bi-layered superstructure. The 1:1 aggregation is further convinced by cross-section TEM observation (Fig. 2c). As comparison, in co-solvents for example ethanol no aggregation is found but individual nanosheet (Fig. 2d). Trisodium citrate capped Fe_3O_4 nanoparticles can be absorbed exclusively onto the ionic liquid side (Fig. 2e), whilst the other side remains smooth. The Fe_3O_4 contained IL based Janus composite nanosheets preserve the Janus performance. They can be simply manipulated with a magnet (Fig. 2f).

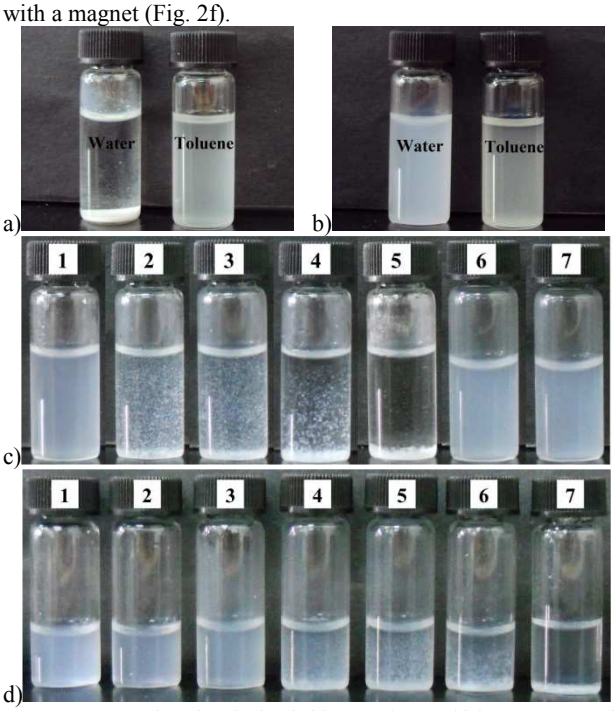


Figure 3. a) PF_6^- based IL-hydrophobic nanosheets which are aggregated in water (left) and dispersible in toluene (right); b) BF_4^- based IL-Janus nanosheets which are dispersible both in water (left) and in toluene (right); c) Janus-hydrophobic reversible transformation of the representative Cl- based IL-Janus nanosheets. 6 μmol of KPF_6 is added into the aqueous dispersion after varied time (min): (1) 0, (2) 2, (3) 5, (4) 8, (5) 10; and 6 μmol of NaCl is added in the system (c5) after varied time: (6) 20 s, (7) 1 h; d) Janus-hydrophobic transformation of the Cl^- based IL-Janus nanosheets with varied feeding amount of KPF_6 (μmol): (1) 0, (2) 2, (3) 4, (4) 4.5, (5) 5, (6) 5.5, (7) 6. All the samples stand for 10 min.

Composition of the IL layer is tunable by simple exchanging anions, meanwhile wettability of the layer is reversibly switchable between hydrophilic and hydrophobic. As an example, after Cl^- is exchanged with PF_6^-, the nanosheets become only dispersible in toluene not in water (Fig. 3a). This reveals that the IL side becomes hydrophobic. After the PF_6^- group is exchanged with BF_4^-, the nanosheets again become dispersible both in oil and water (Fig. 3b). This indicates that Janus performance of the nanosheest has recovered. Morphology of the nanosheets is not influenced by the ion exchange (Fig. S6 a-b). The anion exchanging is general. Along the similar routine, $(CF_3SO_2)_2N^-$, HSO_4^- based IL-Janus nanosheets are derived (Fig. S6 c-f). Presence of the corresponding anionic groups is further confirmed by FT-IR (Fig. S7). The bands at 1650-1550 cm^{-1} are attributed to the imidazolium cation. The bands at 850-840 cm^{-1}, 640-620 cm^{-1}, 1360-1345 cm^{-1}, and 1065-1055 cm^{-1} are attributed to the PF_6^-, HSO_4^-, $(CF_3SO_2)_2N^-$, and BF_4^-, respectively. The

anion exchange degree can be determined by surface XPS element analysis (Fig. S8). For example, presence of F and B elements is verified by XPS spectrum of the BF_4^- based IL-Janus nanosheets, whilst the Cl signal disappears completely. This indicates that the anion exchange has completely achieved.

The anion exchange process is fast (Fig. 3c). As an example, upon feeding 6 μmol of KPF6 into the Cl^- based IL-Janus nanosheet aqueous dispersion, no Cl can be detected onto the nanosheets shortly after feeding KPF_6 within 20 s.[30] The Janus nanosheets start to aggregate and progressively precipitate within minutes (Fig. 3c1-5). When 6 μmol of NaCl is fed into the above precipitation system under shaking, the nanosheets become redispersible in water within 20 s (Fig. 3c6). The dispersion keeps stable over hours (Fig. 3c7). This is consistent with the fast exchange of PF_6^- with Cl^-. Since anion exchange degree is tunable, wettability of the ionic liquid side thus dispersibility of the nanosheets can be controlled (Fig. 3d). As an example, after KPF_6 is fed into the Cl^- based IL-Janus nanosheet aqueous dispersion at varied amount, dispersibility is monitored to evaluate the wettability. At low level below 4 μmol, the IL-Janus nanosheets remain well dispersible in water. This is understandable that a majority of Cl^- is preserved and hydrophilic performance of the IL side dominates. The XPS result reveals that Cl^- and PF_6^- fractions are comparable (Table S1). At an increased level of KPF_6 above 4.5 μmol, PF_6^- dominates within the IL layer. The IL-Janus nanosheets precipitate from the aqueous dispersion. This indicates that the hydrophobic performance dominates. With the increase in KPF_6 feeding amount, the precipitation becomes faster. At high level of for example 6.0 μmol, the nanosheets precipitate completely. SEM observation of the nanosheets in dispersion further confirms the aggregation with PF_6^- feeding amount (Fig. S9). The hydrophobic PF_6^- based IL-Janus nanosheets could be well dispersible in toluene. After drying, individual nanosheets are observed rather than aggregation (Fig. S10).

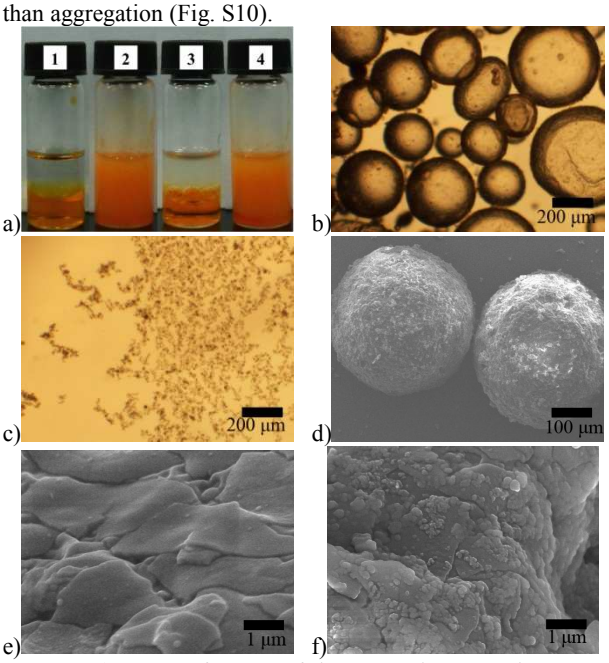


Figure 4. a) Janus performance of the IL-nanosheets as anion responsive surfactants: (1) an immiscible mixture of decane (top) and water (bottom), methyl orange is added to water as chromogenic agent; (2) oil-in-water emulsion stabilized with the Cl^- based IL-Janus nanosheets, decane/water volume ratio is 3:2; (3) after feeding 10 μmol of KPF_6 in the emulsion (2), the emulsion destabilizes; (4) after feeding Cl^- again in the mixture (3), an emulsion forms; b) optical microscopy image of the decane-in-water emulsion (a2); c) optical microscopy image of the middle interface region in (a3); d) SEM image of the dispersed paraffin particles stabilized with the Cl^- based IL-Janus nanosheets, orientation of the Janus nanosheets is frozen at the interface after paraffin is cooled; e, f) magnified SEM images of the paraffin particle surface before and after being labelled with trisodium citrate capped Fe_3O_4 nanoparticles.

Let's demonstrate the representative Cl^- based IL-Janus nanosheets as a solid surfactant to emulsify immiscible liquids (Fig. 4a1) and anion triggered de-emulsification. As an example, an oil-in-water (o/w) emulsion forms at a decane/water volume ratio 3:2 (Fig. 4a2). The emulsion keeps stable over months. A trace amount of methyl orange is added into water phase for easy observation. The dispersed droplets are 100-500 μm in diameter (Fig. 4b), whose size decreases with the Janus nanosheet content. After drops of KPF_6 aqueous solution are added, the emulsion starts to de-emulsify within minutes. Water and oil separate into two immiscible layers eventually (Fig. 4a3). No droplets are observed but fragmental pieces (Fig. 4c). In comparison, in the case of imidazolin based Janus nanosheets, the emulsion keeps stable (Fig. S11a) even after KPF_6 is added. This means that only IL functionalized Janus nanosheets are ion responsive. If KCl is added instead of KPF_6, the emulsion remains stable (Fig. S11b). This suggests that the IL-Janus nanosheets are responsive selectively to anions. After drops of NaCl aqueous solution are added, the immiscible liquids after phase separation become emulsified again in minutes, forming a stable emulsion (Fig. 4a4). It is noted that the anion triggered reversible transformation between emulsification and de-emulsification occurs without stirring if the continuous phase is aqueous. If oil phase is continuous, stirring is required to drive the transformation (Fig. S12). In order to observe orientation of the IL-Janus nanosheets at the interface, a melt-paraffin (Tm: 52~54 °C) is emulsified in water using the Cl^- based IL-Janus nanosheets (Fig. 4d). After the emulsion is cooled down to room temperature, orientation of the IL-Janus nanosheets at the emulsion interface is frozen thereby (Fig. 4e). The nanosheets lay onto the interface. Trisodium citrate capped Fe_3O_4 nanoparticles are used to label the IL-Janus nanosheets. The coarsened side corresponding to the IL group terminated side faces the external aqueous phase (Fig. 4f).

In summary, we report a facile and universal method to synthesize ionic liquid functionalized Janus nanosheets. Wettability of the IL terminated side is triggered between hydrophilic and hydrophobic by anion exchanging. Accordingly, dispersibility of the nanosheets and stability of the emulsion with the IL-Janus nanosheets is triggered by anion exchanging in a reversible way. The transformation can be achieved regardless if the continuous phase is aqueous or oil. The idea can be extended to other IL-based Janus nanosheets with tunable cations.

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Notes and references

[a] *State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences ,Beijing 100190, China. Fax: 8610-62559373; Tel: 8610-82619206; E-mail: yangzz@iccas.ac.cn (Z.Y)*

[b] *Liaoning Provincial Key Laboratory for Green Synthesis and Preparative Chemistry of Advanced Materials (Liaoning University), Shenyang 110036, China. Fax: 8624-62202380; Tel: 8624-62202378; E-mail: songlab@lnu.edu.cn (X. S)*

† Electronic Supplementary Information (ESI) available: Experimental section and supplimental figures. See DOI: 10.1039/b000000x/

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30 The samples for XPS measurement of the anion exchange degree were separated and purified by centrifugation after adding the salt. At a given centrifugation speed (6000 r / min), it took at least 20 s for the separation even upon adding the salt.