Flexible Responsive Janus Nanosheets

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1. Experimental

1.1 Materials

3-mercaptopropyltrimethoxysilane, octadecyltrichlorosilane were purchased from Acros. Maleic anhydride and AIBN were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. Toluene was refluxed over sodium and benzophenone and distilled. DMF was dried and distilled under reduced pressure. Unless specified otherwise, all reagents were used as received.

1.2 Synthesis of 3-butyldianhydride mercaptopropyl trimethoxysilane (BDMPS) [1]

Maleic anhydride (0.49 g), 3-mercaptopropyltrimethoxysilane (0.98 g), AIBN (0.098 g) and DMF (3 mL) were added. The reaction was initiated under UV irradiation for 4 h. After evaporation of the solvent, the sample was preserved in a vacuum dryer.

1.3 Formation of SAM of BDMPS onto $CaCO_3$ particle

After $CaCO_3$ particle (1 g) was dispersed in 12 mL of toluene, BDMPS

(20 mg) solution in 1 mL of toluene was added (namely 2 wt.-%). The mixture was stirred at 400 rpm for 24 h at room temperature. Afterwards, excess of BDMPS was removed by centrifugation and wash with toluene three times, dried in vacuum. A self-assembled monolayer of BDMPS was formed onto the particle surface.

1.4 Surface sol-gel of the BDMPS SAM onto $CaCO_3$ particle

1.0 g of SAM/$CaCO_3$ particle particle was dispersed in 15 mL of ethanol. After 30 min, 20 mL of aqueous ammonia was added. After the mixture was stirred at 400 rpm for 24 h at room temperature, the system was centrifugated and washed with ethanol three times, dried in vacuum. Silica Janus monolayer was achieved onto the particle surface.

1.5 Selective modification of the silica based Janus monolayer

1.0 g of silica based Janus monolayer coated $CaCO_3$ particle was dispersed in 15 mL of toluene. 60 μL of octadecyltrichlorosilane was added. The mixture was refluxed at 80 ºC for 8 h. After cooling to room temperature, the dispersion was centrifugated and washed with toluene three times, dried in vacuum. Silica composite Janus monolayer was derived.

1.6 Acid etching $CaCO_3$ particle

At 50 ºC, 1M HCl aqueous solution (5 mL) was added to the silica Janus composite monolayer coated $CaCO_3$ particle (500 mg) under ultrasonication. After cooling to room temperature, the dispersion was

centrifugated and washed with water three times, dried in vacuum. The carboxyl/alkyl composite Janus nanosheets were derived.

1.7 Labeling the carboxyl/alkyl composite Janus nanosheets with Fe_3O_4 nanoparticles[2]

1.0 mg of the carboxyl/alkyl composite Janus nanosheets was dispersed in water. A small amount of positively charged Fe_3O_4 nanoparticles (10 nm in diameter) was added to the dispersion under stirring for 12 h for a selective labeling. The nanosheets were centrifugated and washed with water.

1.8 pH response of the carboxyl/alkyl composite Janus nanosheets

The carboxyl/alkyl composite Janus nanosheets were dispersed in water at two representative pH levels of 8 and 3, respectively. After the mixture was vigorously shaken, the mixture stood for observation.

1.9 Emulsification with the carboxyl/alkyl composite Janus nanosheets

10 mg of the carboxyl/alkyl composite Janus nanosheets was added in 5 g of water at pH=8. At 70 ºC, a certain amount of paraffin (Tm=52-54 ºC) was added. After the mixture was vigorously shaken, the mixture was cooled to room temperature and stood forming a paraffin-in-water emulsion.

1.10 Labeling the paraffin sphere surface with the Fe_3O_4 nanoparticles

A small amount of positively charged Fe_3O_4 nanoparticles (10 nm in diameter) was added to the emulsion. After standing for 24 h, the system was centrifugated and washed with water at pH=8.

1.11 Characterization

In order to avoid aggregation among the Janus nanosheets, ethanol was used as a dispersant. Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) measurements were performed with a HITACHI S-4800 apparatus operated at an accelerating voltage of 15 kV. AFM images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating at a tapping mode. FT-IR spectroscopy was performed using a Bruker EQUINOX 55 spectrometer with the sample/KBr tablets. Polarizing optical microscopy images were performed with an Olympus optical microscope. ZetaSizer 3000 HS (Malvern Instruments, UK) was used to measure Zeta potential.

2. Results and Discussion

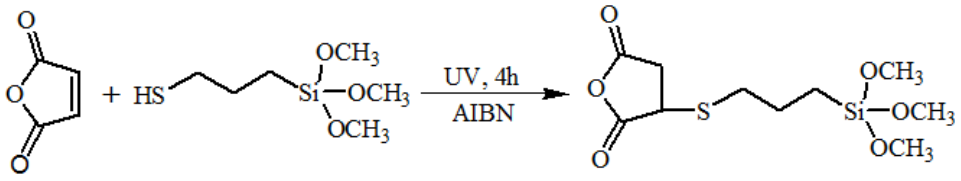

Figure S1. Synthetic route of BDMPS.

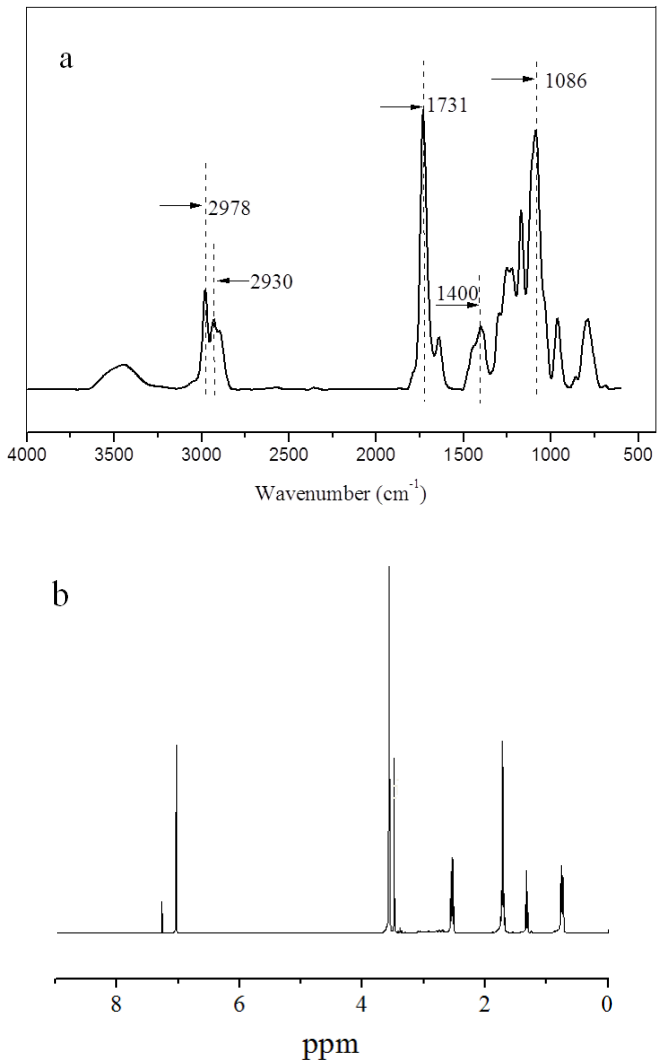

Figure S2. (a) FT-IR spectrum of BDMPS. The peaks at 2978 cm^{-1} and 2930 cm^{-1} assigned to -CH_3 and -CH_2, the peak at 1718 cm^{-1} assigned to -CO, the peak at 1400 cm^{-1} assigned to -S-CH_2-, the peak at 1086 cm^{-1} assigned to -Si-O-Si-.

(b) ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.03(s, 2H), 3.57 (s, 9H, -CH_3), 3.48 (s, 1H), 2.57-2.51 (m, 2 H, -CH_2), 1.76-1.68 (m, 2 H, -CH_2), 0.77-0.73 (m, 2 H, -CH_2).

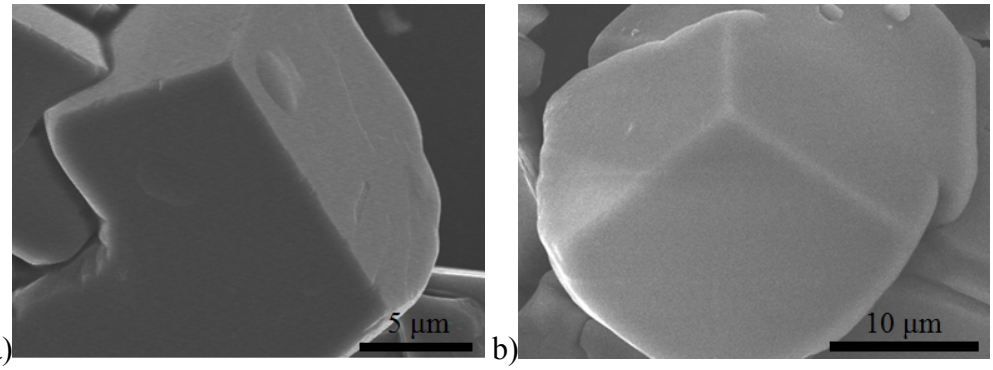

Figure S3. SEM images of the $CaCO_3$ particle surface before (a) and after (b)

absorption of BDMPS at 2 wt.-%.

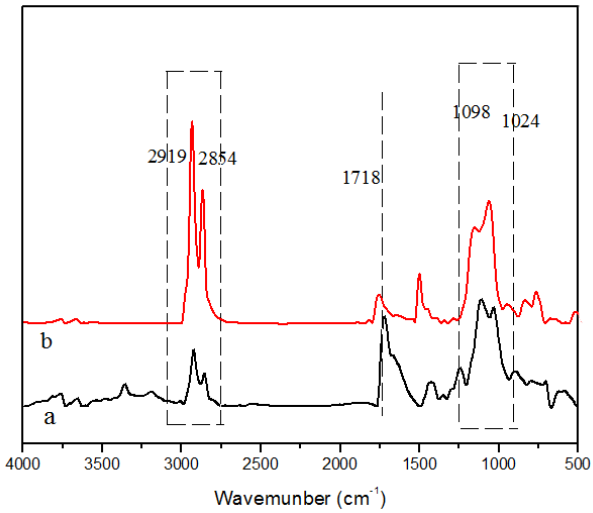

Figure S4. FT-IR spectra of the representative samples: silica Janus nanosheets (a), and the carboxyl/alkyl composite Janus nanosheets (b). In curve (a), the peaks at 1024 cm^{-1} and 1098 cm^{-1} assigned to -Si-O-Si-, the peaks at 2919 cm^{-1} and 2854 cm^{-1} assigned to $-CH_2$, the peaks at 1237 cm^{-1} and 1422 cm^{-1} assigned to $-S-CH_2-$, the peak at 1718 cm^{-1} assigned to -COOH. In curve (b), ratio of $-CH_2$/-Si-O-Si- of the carboxyl/alkyl composite Janus nanosheets higher than the silica Janus nanosheets.

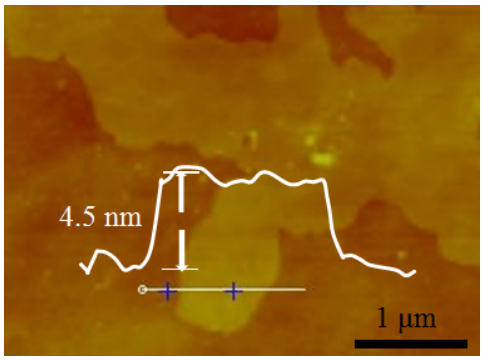

Figure S5. AFM image of the carboxyl/alkyl composite Janus anosheets, 4.5±0.2 nm thick.

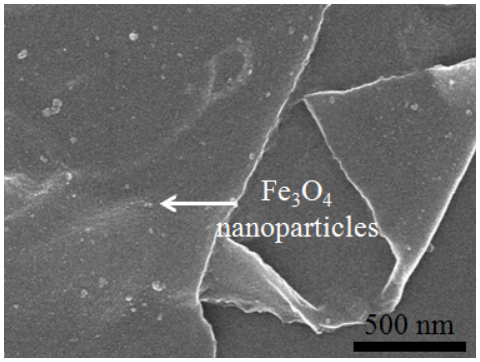

Figure S6. The carboxyl/alkyl composite Janus nanosheets after the positively charged Fe_3O_4 nanoparticles are preferentially absorbed onto the carboxyl- group terminated side.

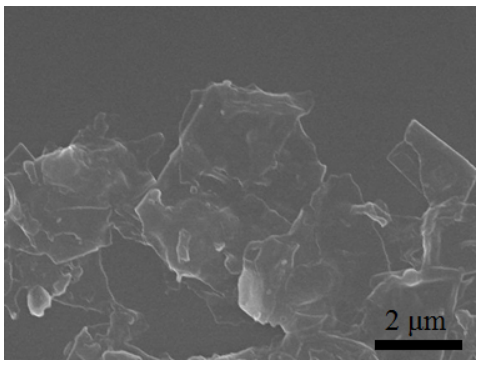

Figure S7. SEM image of the back-to-back stacking bi-layered superstructure of the carboxyl/alkyl composite Janus nanosheets dispersed in toluene.

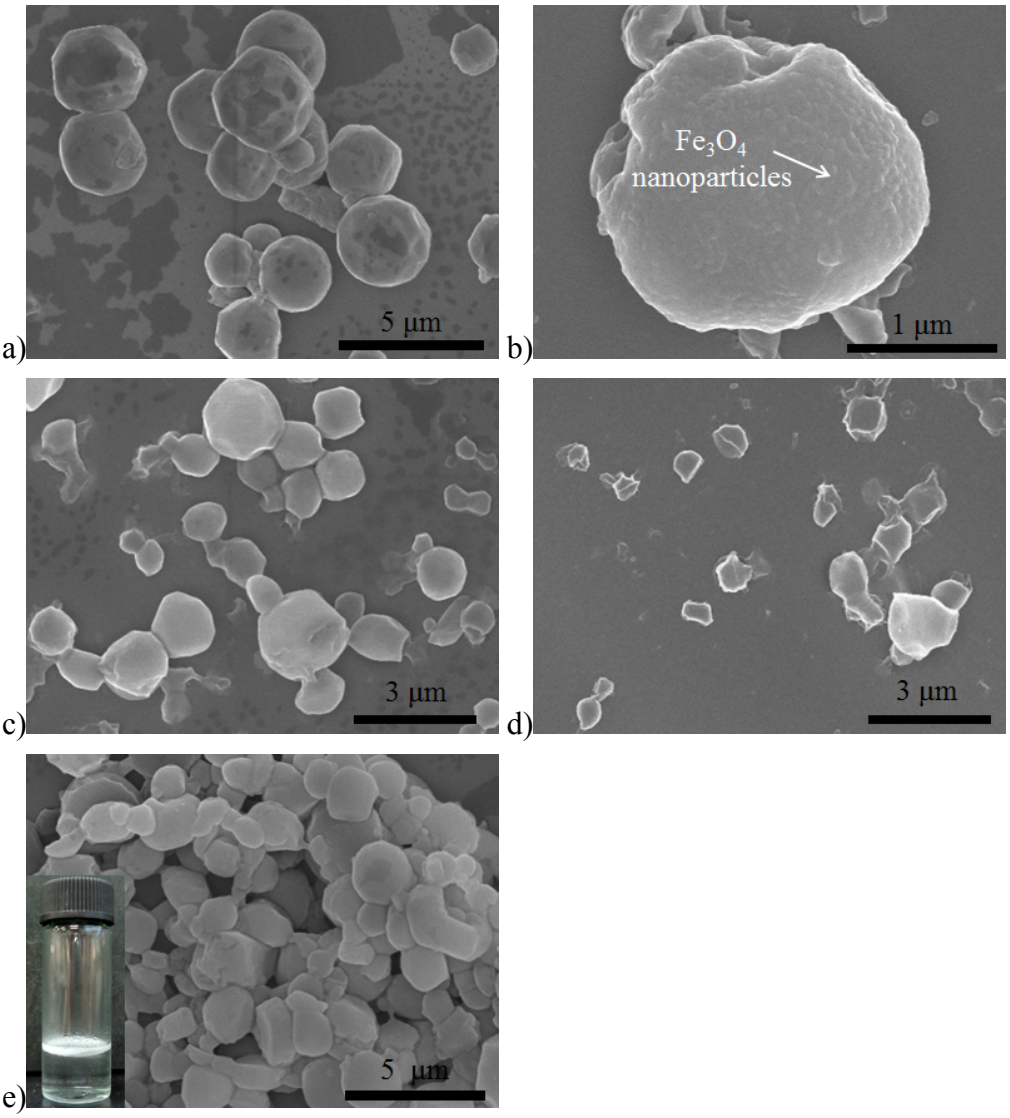

Figure S8. SEM images of the paraffin spheres stabilized with the composite Janus

nanosheets at varied weight ratio of Janus nanosheet/paraffin: 1:100 before (a) and after (b) labeling with Fe_3O_4 nanoparticles; (c) 1:50; (d) 1:10; (e) de-emulsification of the paraffin spheres by adding acid. Water is fixed at 500.

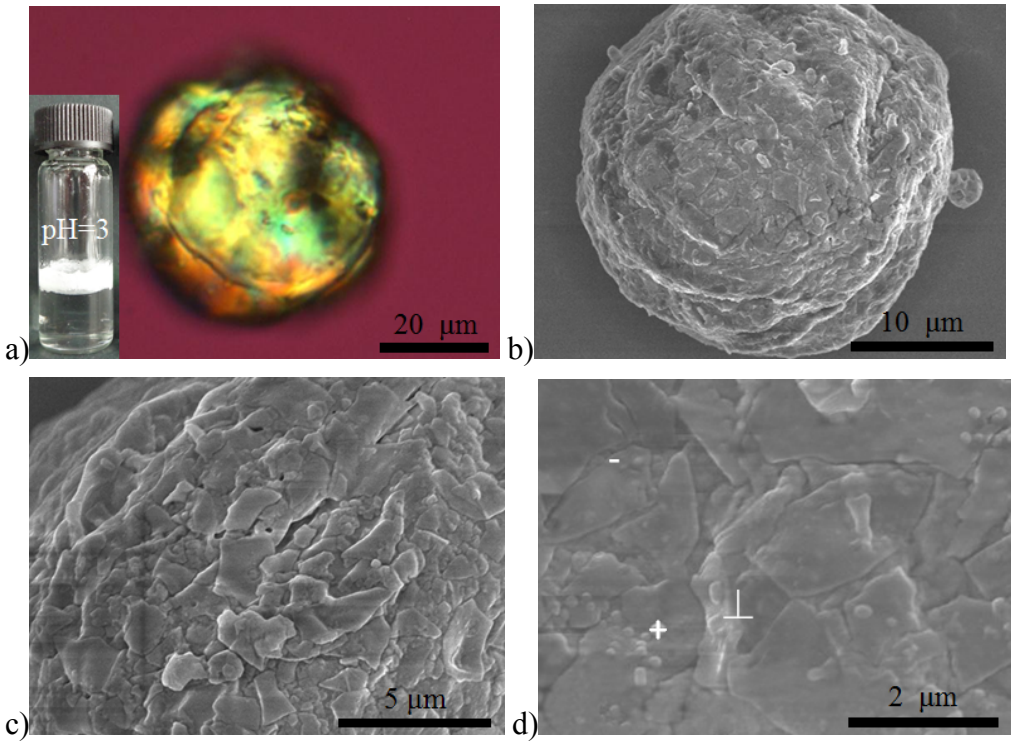

Figure S9. (a) Polarizing optical image of the cooled paraffin-in-water emulsion stabilized with the carboxyl/alkyl composite Janus nanosheets at pH=3, inset photograph of the emulsion; (b, c) SEM images of the paraffin sphere at two magnifications; (d) the paraffin sphere surface after labeling with the Fe_3O_4 nanoparticles. +: the carboxyl- group terminated side, -: the alkyl- group terminated side, ⊥: the nanosheets perpendicular to the surface.

3. Notes and references

1. M. J. Kade, D. J. Burke, C. J. Hawker, J. Polym. Sci., Part A: Polym. Chem. 2010, **48**, 743.
2. C. Tang, C. L. Zhang, J. G. Liu, X. Z. Qu, J. L. Li, Z. Z. Yang, Macromolecules 2010, **43**, 5114.