Supporting Information

Janus Micro-Reactors

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Experiment Detail

1 Materials

Glycol chitosan (GC, M_W~250 kDa), fluorescein isothiocyanate labeled dextran (FITC-dextran, M_W~10 kDa) and 1,1'-dioctadecyl-3,3,3',3'-tetramethylindocarbo-cyanine perchlorate (dil-C18) were purchased from Sigma-Aldrich (St. Louis, US). Benzaldehyde terminated polyethylene glycol (PEG) (M_W~600 Da) was synthesized according to our previous report.[1] N-octyltriethoxysilane (C8-silane) was purchased from Alfa Aesar. TiO_2 nanoparticles (Degussa P25) and poly (ethylene glycol) triethoxysilane (PEG-silane) were purchased from Evonik. Tetraethoxysilane (TEOS), solvents and other compounds were obtained from Beijing Chemical Reagents Company, China.

2 Preparation of P25 contained hollow gel microspheres

The P25 contained hollow gel microspheres were prepared by ultrasonic-spray method.[1] Briefly, 50 mg of GC and 42.5 mg of OHC-PEG-CHO was dissolved in

distilled water, and pH of the solution was adjusted to 4.0 using 2 M aqueous HCl. 2 mg of P25 nanoparticle was dispersed in the polymer solution. The gel microspheres were fabricated by ultrasonic-spraying of the polymer/P25 dispersion using a Sono-Tek ultrasonic nozzle vertically placed on the top of a glass tube with a diameter of 3.5 cm and a length of 35 cm. Ammonia was gassed into the glass tube through a bypath in order to ensure a basic atmosphere. The fog drops were collected in a beaker placed at the bottom end of the tube. The dispersion in the beaker was transferred to a dialysis tube with a molecular weight cut-off of 12 kDa and dialyzed against $NaHCO_3$ solution (pH 8-8.5) at room temperature after six changes in 24 h period, then against distilled water after two changes over 8 h. The dialysate was freeze-dried to harvest a white powder like product with a yield of 80 %. Inorganic content (P25) was measured about 1.85 wt% by TGA.

3 Preparation of silica composite microspheres

20 mg of P25 contained gel microspheres was re-dispersed in PBS (0.01 M pH 7.4) at 1 mg/mL. 215 μL of TOES dissolved in 12 mL of ethanol was added under stirring at room temperature. After stirring for 24 h, the mixture was centrifuged at 12,000 rpm for 1 min. The centrifugate was washed with ethanol for 3 times, and then dried at 80 ^{o}C to harvest a white powder-like product with a yield of 70%. The inorganic content is 58.1 wt% determined by TGA. 1.2 wt% of P25 is confirmed using EDX.

4 Preparation of the Janus micro-reactors

30 mg of silica composite hollow microspheres was dispersed in 20 mL of ethanol. 100 μL of PEG-silane was added under stirring and the mixture was refluxed at 80 ^{o}C for 12 h and cooled down to room temperature before centrifugation at 12,000 rpm for 1 min. The centrifugate was washed with ethanol for 3 times and dried at 80 ^{o}C. The powder-like product of PEG-modified composite hollow microsphere was immersed in aqueous hydrochloric acid (1 M) and shaken for 12 h to remove the gel. The resultant PEGylated silica sphere was separated via centrifugation, washed with distilled water, dried at 80 ^{o}C. The sample was then re-dispersed in 20 mL of ethanol with 100 μL of n-octyltriethoxysilane, and refluxed at 80 ^{o}C for another 12 h. The solid was collected by centrifugation, washed with ethanol and dried at 80 ^{o}C to gain a white powder-like Janus hollow microsphere with a yield of 85%. The inorganic content is determined using TGA and EDX (SiO_2, 55.3 wt%; P25, 0.8 wt%).

5 Characterizations

Fourier transform infrared (FT-IR) spectroscopy was performed using a Bruker Equinox 55 spectrometer with the sample/KBr pressed pellets. Nitrogen adsorption was performed on a Micromeritics ASAP 2020M Surface Area and Porosity Analyzer. Scanning electron microscopy (SEM) was carried out on a HITACHI S-4300 instrument set at 15 kV. Transmission electron microscopy (TEM) was performed using a JEOL 2011 at 200 kV. The samples were embedded in epoxy resin and microtomed into slices about 80-100 nm thick using Leica ultracut UCT

ultramicrotome at room temperature and stained with 0.1% phosphotungstic acid (PTA).

The inorganic content was determined by TGA using a Pyris 1 TGA HT Lab System (Perkin Elmer, US) at a heating rate of 10 ^{o}C min^{-1} from 30 ^{o}C to 700 ^{o}C in air.[2] The TiO_2 (P25) content in the inorganic fraction was measured using energy dispersive X-Ray spectroscopy (EDX) (HITACHI S-4800) on the TGA residues, through a comparison of the silicon/titanium (Si/Ti) molar ratio.[3]

The Janus micro-reactors were characterized using confocal laser scanning microscope (CLSM, Leica TCS-sp2, Germany). The Janus micro-reactor was dispersed in the aqueous solution of FITC-dextran (1 μg/mL) or the cyclohexane solution of dil-C18 (1 μg/mL) for 1 min, collected via centrifugation and then re-dispersed in water. A drop of the water dispersion was pipetted onto a glass microscope slide and mounted with a cover slip. The excitation wavelength was set at 488 nm and the emission wavelength range was 510-600 nm.

Dispersibility of the prepared microspheres in aqueous solution (2 mg/mL) was monitored using ultraviolet spectrophotometer (UV, LN12-TU-109) at an absorbance of 600 nm.[4]

6 Dye adsorption by the Janus micro-reactors

Adsorption capacity. A given amount of the Janus micro-reactor was dispersed in 1 mL of water. A desired volume of cyclohexane was injected to the above aqueous phase with a micro-syringe. The mixture was stirred for 30 sec and stood for 30 min

to observe presence of the upper organic phase onto the bottom aqueous phase. In the case that no organic layer was observed, additional cyclohexane was injected and the observation was followed along the same procedure until the organic phase started to appear. The total volume of the cyclohexane absorbed by the Janus microsphere was thus determined.

Adsorption kinetics. Dil-C18, a hydrophobic dye, was used as a model organic molecule for the adsorption test. Silica microsphere, PEGylated silica microsphere and the Janus microsphere were dispersed in cyclohexane solution of dil-C18 at 10 μg/mL. Solid concentration of the microsphere was fixed at 0.25 mg/mL. After incubation for a desired period, the dispersion was centrifugted. The upper oil phase was monitored with UV-visible spectroscopy to determine the residue dye concentration.

Phase transfer of hydrophobic molecules. Dil-C18 was dissolved in cyclohexane at a concentration of 7.5 μg/mL. The solution (0.5 mL) was mixed with 0.5 mL of water and the mixture was transferred in a glass vial and held for hours (protected from light) for an equilibrated phase separation. 0.125 mg of the Janus micro-reactor was carefully poured into the vial and the vial was generally shaken to ensure that the sample powder was immersed in the top oil. The vial stood for varied period to monitor color change.

Collection of organic compounds from aqueous sorroundings. The aqueous solutions of dil-C18 at two low concentration levels, i.e. 0.1 ppm, and 0.025 ppm, were prepared and mixed with the Janus microsphere at 0.25 mg/mL. After held for 5

min, the microsphere was centrifugated. The dye concentration in water was measured. The above tests were conducted for three times.

Photocatalytic decomposition of dyes in the Janus micro-reactors. The dye loaded Janus micro-reactor (separated by centrifugation) was re-dispersed in distilled water in a quartz pool. The pool was irradiated under an ultraviolet lamp (UVB-313, 40w) for a desired period, e.g. 30 min and 1 h. The microsphere was then collected via centrifugation at 12,000 rpm for 1 min, dried and subjected to FT-IR characterization.

Regeneration of the Janus micro-reactors. The Janus micro-reactor was dispersed in water at a concentration of 0.25 mg/mL, and then an equal volume of dil-C18 cyclohexane stock solution (2.5 μg/mL) was added, stirred and stood for a phase transfer. The aqueous phase was collected in a quartz pool and irradiated by an ultraviolet lamp for 30 min, and then mixed with same amount of dil-C18 cyclohexane stock solution (2.5 μg/mL) and sampled following the same procedure. The experiment was performed for four cycles. In each cycle, the dye concentration in the organic phase was measured.

References

1 L. L. Zhao, L. J. Zhu, Q. Wang, J. L. Li, C. L. Zhang, J. G. Liu, X. Z. Qu, G. L. He, Y. F. Lu, Z. Z. Yang, *Soft Matter* **2011**, *7*, 6144.

2 S. J. Ding, B. Liu, C. L. Zhang, Y. Wu, H. F. Xu, X. Z. Qu, J. G. Liu, Z. Z. Yang, *J. Mater. Chem.* **2009**, *19*, 3443.

3 A. Verket, H. Tiainen, H. J. Haugen, S. P. Lyngstadaas, O. Nilsen, J. E. Reseland, *Biointerphases* **2012**, *7*, 36.

4 C. A. Fernandez, E. M. Hoppes, J. G. Bekhazi, C. M. Wang, R. J. Wiacek, M. G. Warner, G. E. Fryxell, J. T. Bays, R. S. Addleman, *J. Phys. Chem. C* **2008**, *112*, 13947.

Supplementary Figures

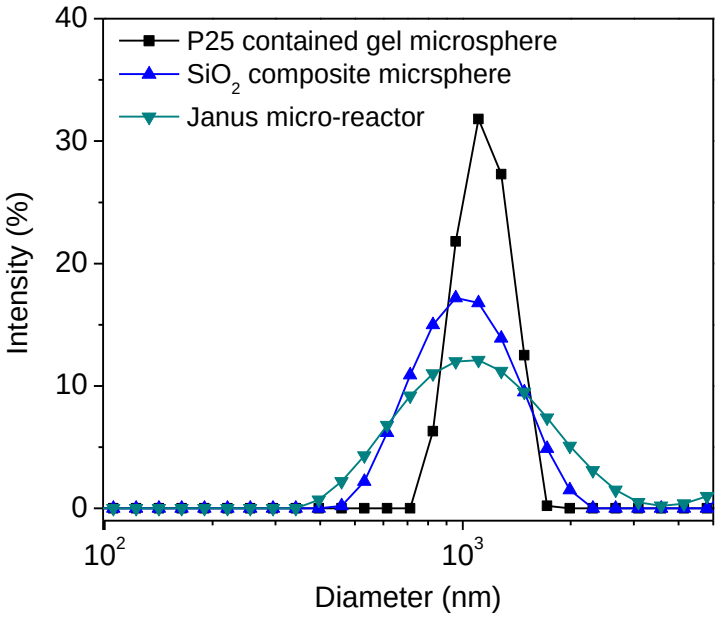
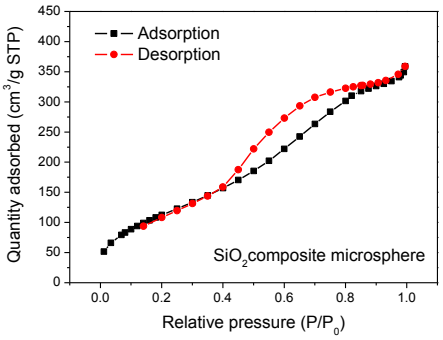
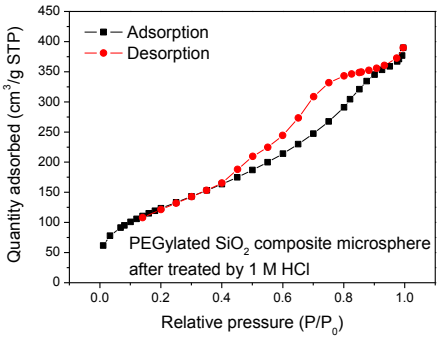


Figure S1. DLS diagram of the P25 contained chitosan/PEG gel hollow microsphere, the SiO_2 composite hollow microsphere and the Janus micro-reactor. The concentration for the DLS measurement is 2 mg/mL.



(a)



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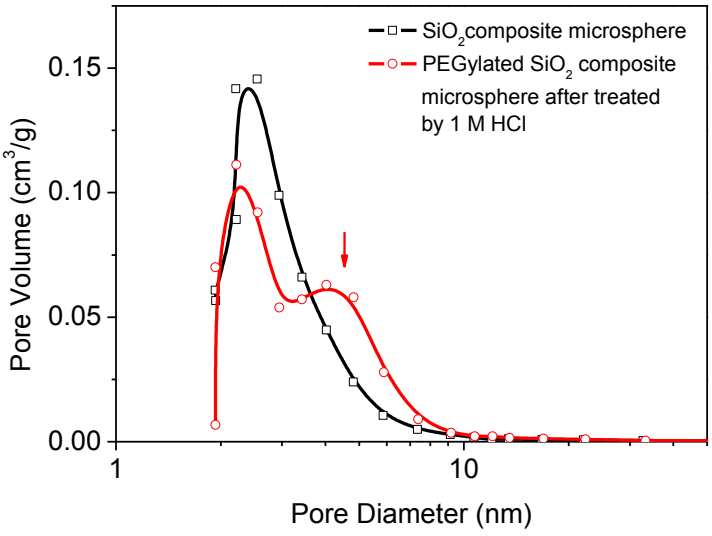

(c)

Figure S2. Nitrogen adsorption/desorption curves (a, b) and the pore size distribution (c) of the SiO_2 composite microsphere and PEGylated silica microsphere after the gel template is dissolved. The pore volume is calculated to be 0.28 and 0.32 cm^3/g, respectively.

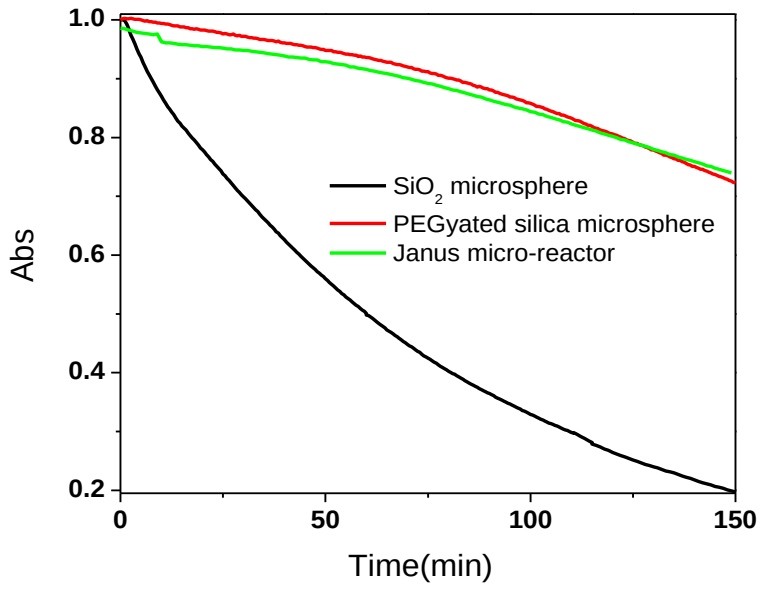

Figure S3. Dispersibility of the SiO_2 composite hollow microsphere, PEGyated silica microsphere and Janus micro-reactor, monitored using UV at 600 nm. The concentration of the dispersion is 2 mg/mL.

Figure S4. Phase transportation of dil-C18 from cyclohexane to water by taking on the Janus micro-reactor. **Left:** Dil-C18 cyclohexane solution over water. **Middle:** Soon after the addition of Janus micro-reactor to the cyclohexane phase of dil-C18 solution, the transparent oil phase becomes turbid. However the microspheres only stay in the oil phase shortly, before they start to settle down to the bottom layer of the oil phase. **Right:** The microspheres transfer into the water phase within 30 min. At this time point, it is noted that the bottom water phase become colourful turbid but homogeneous, whereas the top oil phase appears transparent again. Dash lines indicate the oil/water interface.

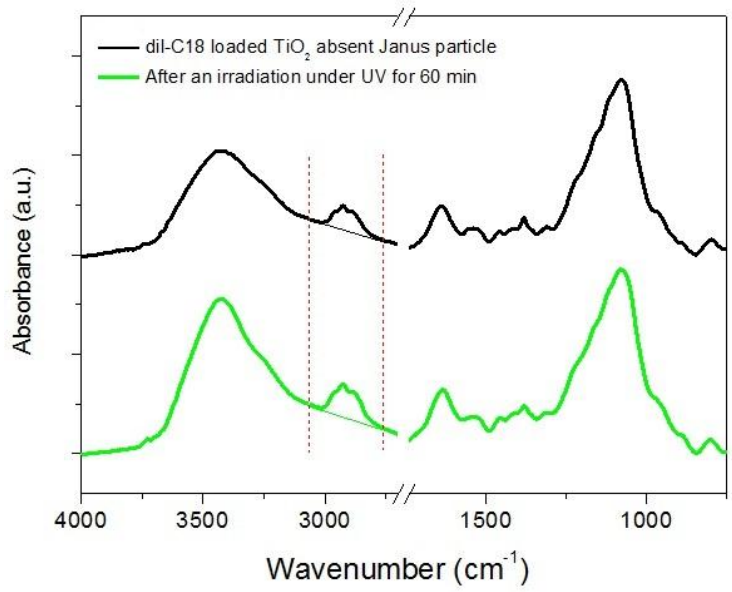

Figure S5. FT-IR spectra of the dil-C18 dye contained Janus micro-reactor without P25 in caves before and after UV irradiated decomposition for 60 min.

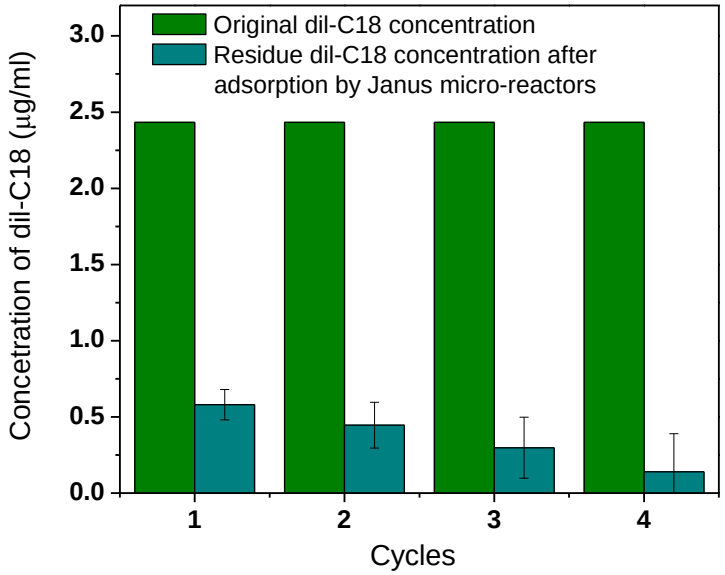

Figure S6. Cycling test of dil-C18 loading and photo decomposition using the Janus micro-reactor. The Janus micro-reactor is dispersed in the mixture of water and cyclohexane containing dil-C18 dye. The micro-reactor is collected via centrifugation, exposed under UV irradiation and then re-dispersed in a fresh water/cyclohexane/dil-C18 mixture for the next cycle.