

Electronic Supplementary Information

A Versatile Colloidal Janus Platform: Surface Asymmetry Control, Functionalization, and Applications

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1. Experimental Section

1.1 Materials

All chemicals were used as received unless otherwise stated. Aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25~28 wt%), ethanol, tetraethyl orthosilicate (TEOS), methylbenzene, trichloromethane, silver nitrate (AgNO_3 , $\geq 99.8\%$), hydrochloric acid (HCl, 36~38 wt%), 4-nitrophenol (4-NP), potassium borohydride (KBH_4), sodium hydroxide (NaOH), trisodium citrate, and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Dichlorodimethylsilane (DCDMS), 3-hydroxytyramine hydrochloride (dopamine hydrochloride) and tris(hydroxymethyl)-aminomethane (Tris) were obtained from Sigma-Aldrich. (3-aminopropyl)triethoxysilane (APTES), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and fluorescein isothiocyanate (FITC) were supplied by Aladdin Industrial Corporation (Shanghai, China). Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was bought from Fuchen Chemical Reagents Factory (Tianjin, China). Paraffin wax (melting point is 52~54 °C) was provided by Shanghai Hualing Rehabilitation Equipment Factory. The qualitative grade filters with maximum pore size 15-20 μm were purchased from Hangzhou special paper Co. Ltd. Ultrapure water (resistivity $> 17 \text{ M}\Omega/\text{cm}$) produced from a GZY-P10 water system was employed throughout the experiments.

1.2 Experiments

1.2.1 Synthesis of SiO_2 Colloidal Particles

Three kinds of spherical SiO_2 colloidal particles with mean diameters of 0.52, 0.88, and 1.25 μm were prepared according to the Stöber method.¹ For example, to synthesize SiO_2 particles with a mean size of 0.51 μm , 160.0 g ethanol and 26.4 g aqueous ammonia were first added to a 500 mL four-necked flask under stirring. Then, a mixture of 63.4 g ethanol and 18.6 g TEOS were fed dropwise by a peristaltic pump. After feeding, the reaction was sustained for the other 24 h prior to completion. The product was rinsed and centrifuged with ethanol several times, and finally dried in vacuum at room temperature for 24 h. Upon increasing the amount of TEOS added, bigger SiO_2 particles with mean sizes of 0.88 and 1.25 μm can be obtained.

1.2.2 Surface Wetting Tuning

The surface wetting property of the SiO_2 particles was tuned by varying the concentration ratio ($C_{\text{APTES}}/C_{\text{DCDMS}}$) between (3-aminopropyl)triethoxysilane (APTES) and dichlorodimethylsilane (DCDMS) in solution. In brief, 0.2 g silica powders were dispersed into 30 g methylbenzene in a 50 mL conical flask. Subsequently, a mixture of APTES and DCDMS was added to the flask under constant magnetic stirring for 2 h. The products were centrifuged and rinsed several times with ethanol, and finally dried in vacuum at room temperature for 24 h. The concentration ratio of the applied APTES and DCDMS affects the wetting property of the particles, and further influences the resident geometry of the particles at the wax/water interfaces. The recipe is summarized in Table 1 and detailed in Table S1.

1.2.3 Pickering Emulsions

The surface-modified SiO_2 particles obtained from section 1.2.2 were used to construct oil-in-water Pickering emulsions. Typically, 0.2 g SiO_2 powders were added in a 50 mL beaker containing 10 mL of ultrapure water and 1 g paraffin wax at 75 °C. By the time the wax

melted, the mixture was homogenized with an IKA T18 homogenizer at a speed of 9000 rpm for 3 min. After cooling the system to room temperature, the solid wax droplets were filtered and rinsed with water with the assistance of a water-circulating-vacuum pump. The products (wax-SiO₂) were stored in 5 mL deionized water with a concentration of about 0.16 g/mL.

1.2.4 Polydopamine Coating

First, 0.5 mL (0.16 g/mL) of as-synthesized wax-SiO₂ Pickering emulsions was added to 100 mL Tris-Buffer (0.1 M, pH = 8.5) under stirring. Second, 0.05 g dopamine monomer was added into the mixture, and the mixture was incubated at 25 °C for 1 h. Third, the products were filtered and rinsed with water. Finally, the products (wax-SiO₂/polydopamine PDA) were stored in 5 mL deionized water for the subsequent use.

For the synthesis of SiO₂/PDA Janus particles, chloroform was employed as the good solvent to dissolve paraffin wax. The well-defined SiO₂/PDA Janus particles were yielded.

1.2.5 Synthesis of SiO₂/PDA-Ag Janus Particles

PDA can *in-situ* reduce Ag⁺ ions to Ag nanoparticles without any assistance from extra reductants because it is abundant in catechol and amino groups.^{2,3} In short, 40 mL Ag precursor aqueous solution ([Ag(NH₃)₂]⁺ ions, 2 mg/mL) was first freshly prepared by feeding aqueous ammonia dropwise into the AgNO₃ solution. Then, 5 mL wax-SiO₂/PDA aqueous suspension (0.17 g/mL) was added to the [Ag(NH₃)₂]⁺ -ion aqueous solution under stirring. The reaction was complete in 1 h. The products (wax-SiO₂/PDA-Ag) were filtered and rinsed with water, and the SiO₂/PDA-Ag Janus particles were obtained after the removal of paraffin wax with chloroform.

1.2.6 Synthesis of SiO₂/PDA-Fe₃O₄ Janus Particles

Making use of the adhesive PDA coatings, we managed to link trisodium citrate-coated Fe₃O₄ nanoparticles with SiO₂/PDA Janus particles. First, Fe₃O₄ nanoparticles were synthesized through the co-precipitation of Fe²⁺ and Fe³⁺ ions in the aqueous phase. In detail, 100 mL NaOH aqueous solution (5 M) was placed into a 250 mL three-necked flask under stirring in N₂. Then, 10 mL FeCl₃ (1 M) and 11 mL FeCl₂ (0.5 M) aqueous solutions were mixed and added to deoxygenated NaOH solution. The mixture was stirred for 1 h at 25 and 90 °C, sequentially. 100 mL trisodium citric aqueous solution (0.3 M) was added thereafter to the mixture and the stirring was continued for another 30 min. After precipitating with acetone and rinsing with water, Fe₃O₄ nanoparticles with a mean size of 6.37 nm (the inset in Fig. 3c-i) were obtained.

By simply mixing the Fe₃O₄ nanoparticle (20 mL, 0.7 mg/mL in water) with wax-SiO₂/PDA particles (5 mL, 0.17 g/mL) at room temperature for 24 h, nanoparticles were directed to the PDA coatings, probably associating to the affluent catechol and amino groups of the PDA coatings though the mechanism is not fully understood. After the removal of the wax phase, SiO₂/PDA-Fe₃O₄ Janus particles were yielded.

1.2.7 Synthesis of SiO₂/PDA-FITC Janus Particles

The graft of fluorescein isothiocyanate (FITC) to PDA can be achieved via Michael reaction.⁴ Similar to the previous procedure, this time, 0.5 mL wax-SiO₂/PDA (0.17 g/mL) suspension was added into 12 mL ethanol consisting of 1 mg FITC, followed by stirring at room temperature for 24 h. Note that the reaction was carried out in dark to minimize the bleaching of the dye. The SiO₂/PDA-FITC Janus particles were obtained after the removal of paraffin wax.

In addition, the experiments mentioned above were executed by using SiO₂ particles with a mean size of 0.52 μm as the matrix. Using big SiO₂ particles, e.g., 0.88 μm and 1.25 μm, retained the similar results to those from 0.52 μm sized SiO₂ particles. In other word, the method to synthesize colloidal Janus particles is generic, regardless of the size of the colloidal matrixes applied.

1.2.8 Application Demonstration in Wastewater Treatment

To mimic the wastewater, 600 μL oil red-dyed toluene was mixed with 40 mL deionized water that was stained with 4-NP. After the addition of the SiO₂/PDA-Ag Janus particles (1 mL, 10 mg/mL aqueous suspension), the toluene/water interfaces were stabilized by Janus particles, forming stable Pickering emulsions. The unattached Janus particles can be removed by centrifugation. The introduction of 0.216 g KBH₄ led to a gradual degradation of 4-NP catalyzed by the Janus particles, reducing the yellow color of the water phase finally to transparent. The degradation of 4-NP in water phase was monitored by using a UV-Vis spectrophotometer with a 3-minute interval. The oil phase was removed by centrifugation prior to the measurement.

In addition, to demonstrate the application in oil enrichment from the aqueous phase, SiO₂/PDA-Fe₃O₄ Janus particles were introduced to an oil-water mixture where toluene was used as the oil phase. Upon manually shaking for several minutes, SiO₂/PDA-Fe₃O₄ Janus particles can stabilize the oil phases, forming Pickering emulsions. Due to the Fe₃O₄ nanoparticles decorated, oil phase can be collected with a magnet.

1.3 Characterization

Scanning electron microscopy (SEM) analysis was used to observe the surface details of the particles and carried out using a Hitachi SU-8020 field emission scanning electron microscope (Japan) at a voltage of 1 kV. All samples were diluted with ethanol and attached to silica wafers with a double-sided tape made on electricity-conductive carbon. Transmission electronic microscopy (TEM) images, energy dispersive spectra (EDX) and mapping results were obtained using a FEI Tecnai G2 F20 field emission transmission electronic microscopy (U.S.A.). All samples were diluted with ethanol and ultrasonicated at 25 °C for 10 min, and then dropped onto carbon-coated copper grids prior to observation. The average diameters of the SiO₂ particles were obtained based on the measurement of more than 100 particles from TEM images. The emulsions were imaged with a Nikon Ti-U inverted microscopy (Japan). Water contact angle was measured using a Dataphysics OCA 20 optical contact-angle meter (Germany) equipped with a camera at ambient temperature. 2 μL of deionized water was dropped onto the samples using an automatic dispenser. Average contact angle values were obtained by measuring the sample at six different positions, and the images were captured with a camera. FITC labeled emulsions and Janus particles were imaged on an Olympus FV1200 confocal laser scanning microscope (Japan) equipped with a fluorescein isothiocyanate (FITC) filter cube with an excitation wavelength of 488 nm.

Fourier-transform infrared spectra were performed on a Bruker EQUINOX55 Transform Infrared Spectra (Germany). All samples were centrifuged and rinsed with ethanol. They were dried in a vacuum oven for 24 h and pressed into KBr pellets prior to the examination. The spectra were taken from 4000 to 400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS Ultra X-ray photoelectron spectrometer (Kratos Analytical, U.K.) equipped with a monochromatized Al Kα X-ray source (1486.6 eV) as the excitation source. The containment carbon (C 1s = 284.6 eV) was used to calibrate all binding energies. X-ray powder diffraction (XRD) spectra were acquired by using a DX-2700 X-ray diffractometer (China) equipped with a Cu tube and a diffracted

beam curved graphite monochromator operating at 40 kV and 30 mA. X-Ray diffraction patterns were obtained by scanning the samples at a rate of 0.02 °/s in the range of 10° - 90° (2θ). UV-Vis spectra were collected using a Lambda UV-Vis spectrophotometer (PerkinElmer, U.S.A.) equipped with a temperature controller. The absorbance spectra were recorded at room temperature with the wavelength taken from 200 to 600 nm. The zeta potential measurement was performed on a Delsa Nano C apparatus (Beckman Coulter, U.S.A.). The magnetic properties of the samples were determined by using an LDJ 9600 vibrating sample magnetometer (U.S.A.) with a maximum field of 3 T at room temperature.

2. Supplementary Figures and Table

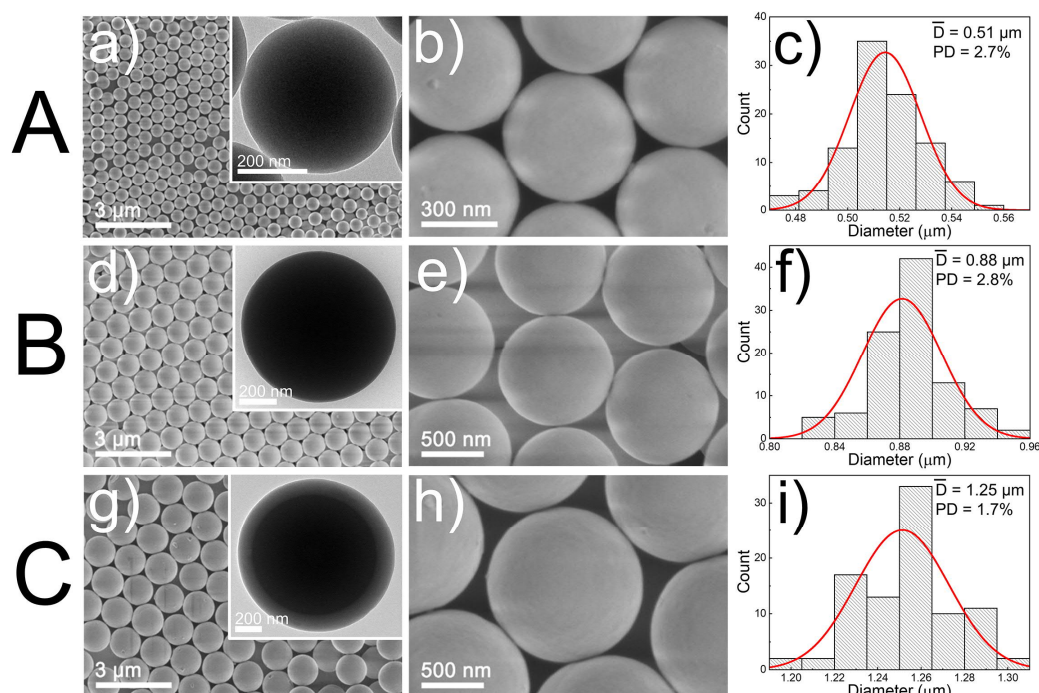


Fig. S1 Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and size distribution analyses of SiO_2 colloidal matrix particles. Three batches of monodisperse SiO_2 particles with mean sizes from 0.51 (batch A), to 0.88 (batch B), and further to 1.25 μm (batch C) are employed. In general, the SEM images in the first column (a), (d), and (g) are the overview of the samples, the second column (b), (e), and (h) shows the magnified SEM images, the third column (c), (f), and (i) exhibits the size distribution histograms and their normal fittings, and the insets in the first column are transmission electron microscopy (TEM) observations, for each batch, respectively.

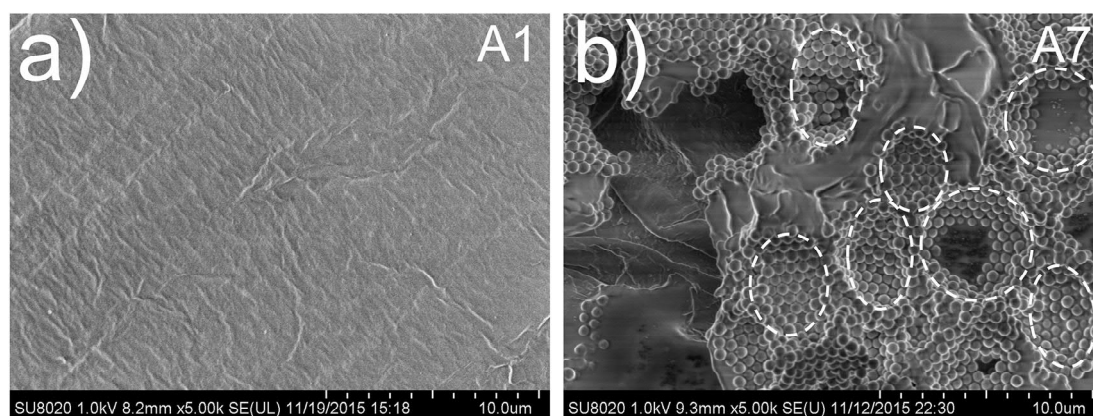


Fig. S2 SEM observations of surfaces of solid wax in the presence of particles A1 (a) and A7 (b). The particles A1 and A7 are treated following the recipes shown in Table S1. The pristine SiO_2 particles (A1) are superhydrophilic (the particles favor staying in the aqueous phase), while the DCDMS-treated SiO_2 particles (A7) are highly hydrophobic, both of which are not capable of stabilizing oil-in-water Pickering emulsions. The white dash circles indicate the voids where water droplets located.

Table S1. The detailed recipes applied for modifying the surface of the SiO₂ particles

Sample number	C_{APTES} (M)	C_{DCDMS} (M)	C_{APTES} / C_{DCDMS}
A1	-	-	-
A2	0.354	-	-
A3	0.354	0.0225	1:0.0636
A4	0.354	0.0674	1:0.191
A5	0.354	0.135	1:0.381
A6	0.354	0.225	1:0.636
A7	-	0.225	-

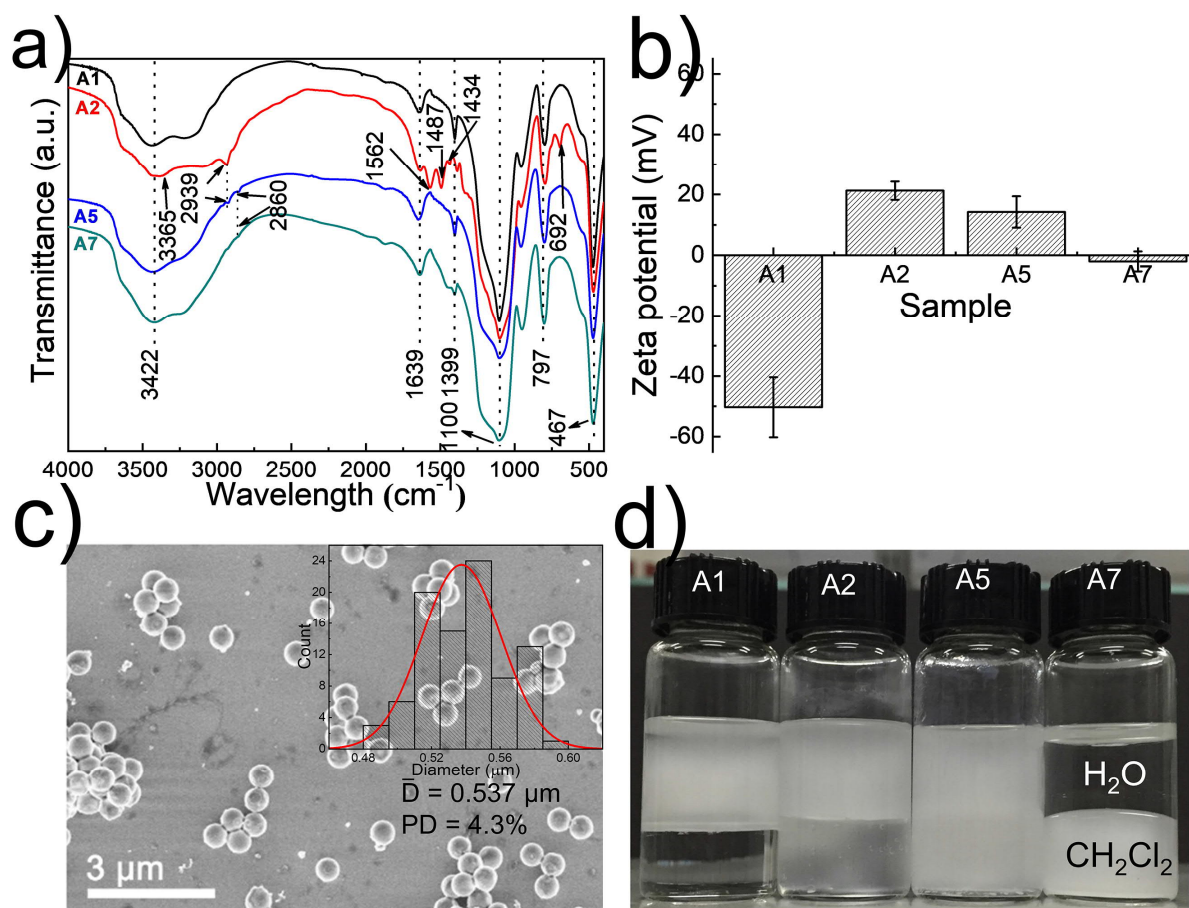


Fig. S4 Characterization of SiO₂ colloidal particles: (a) Fourier transform infrared (FTIR) spectra of sample A1 (pristine SiO₂ particles), A2 (APTES-modified SiO₂ particles), A5 (APTES-DCDMS-modified SiO₂ particles) and A7 (DCDMS-modified SiO₂ particles) shown in Table 1 and Table S1. Six absorption bands at 3422, 1639, 1399, 1100, 797, 467 cm⁻¹ are observed in all samples as the dash lines marked, which correspond to O-H stretching, H-O-H bending, -C-H (-CH₂-) bending and Si-O-Si asymmetric stretching, bending and Si-O-Si symmetric stretching vibrations, respectively.^{5,6} Two bands presented in the region of 3300-3500 cm⁻¹ (3365 and 3422 cm⁻¹), and the peaks at 2939, 1562, 1487, 1434, and 692 cm⁻¹ in A2 may be ascribed to N-H (primary amine) stretching, C-H stretching, N-H bending, -NH₂ scissoring, -CH₂- deformation, and N-H wagging vibrations, respectively, indicating a successful surface graft of APTES. In addition, 2860 cm⁻¹ shown in A7 is the symmetric bending vibration from the -CH₃ group, which may derive from DCDMS. The spectrum of A5 combines these characteristic peaks from A2 and A7, suggesting an integrated surface modification with both APTES and DCDMS; (b) Zeta potential measurement of samples A1, A2, A5, and A7. The potential of A5 is an intermediates between those of A2 and A7, providing a strong evidence of the co-grafting of APTES and DCDMS (c) SEM image of sample A5. The inset is the size distribution and its normal fitting. The APTES-DCDMS coating thickness is calculated to be ca. 13.5 nm; (d) Photographs of dispersibility measurement of samples A1, A2, A5, and A7 in water and dichloromethane (CH₂Cl₂). While A1 and A2 prefer staying in the water phase, A7 stays in the oil phase. A5 can disperse in both water and oil phase, exhibiting a combined wetting property of those of A2 and A7. All results corroborate the data shown in Fig. 2c.

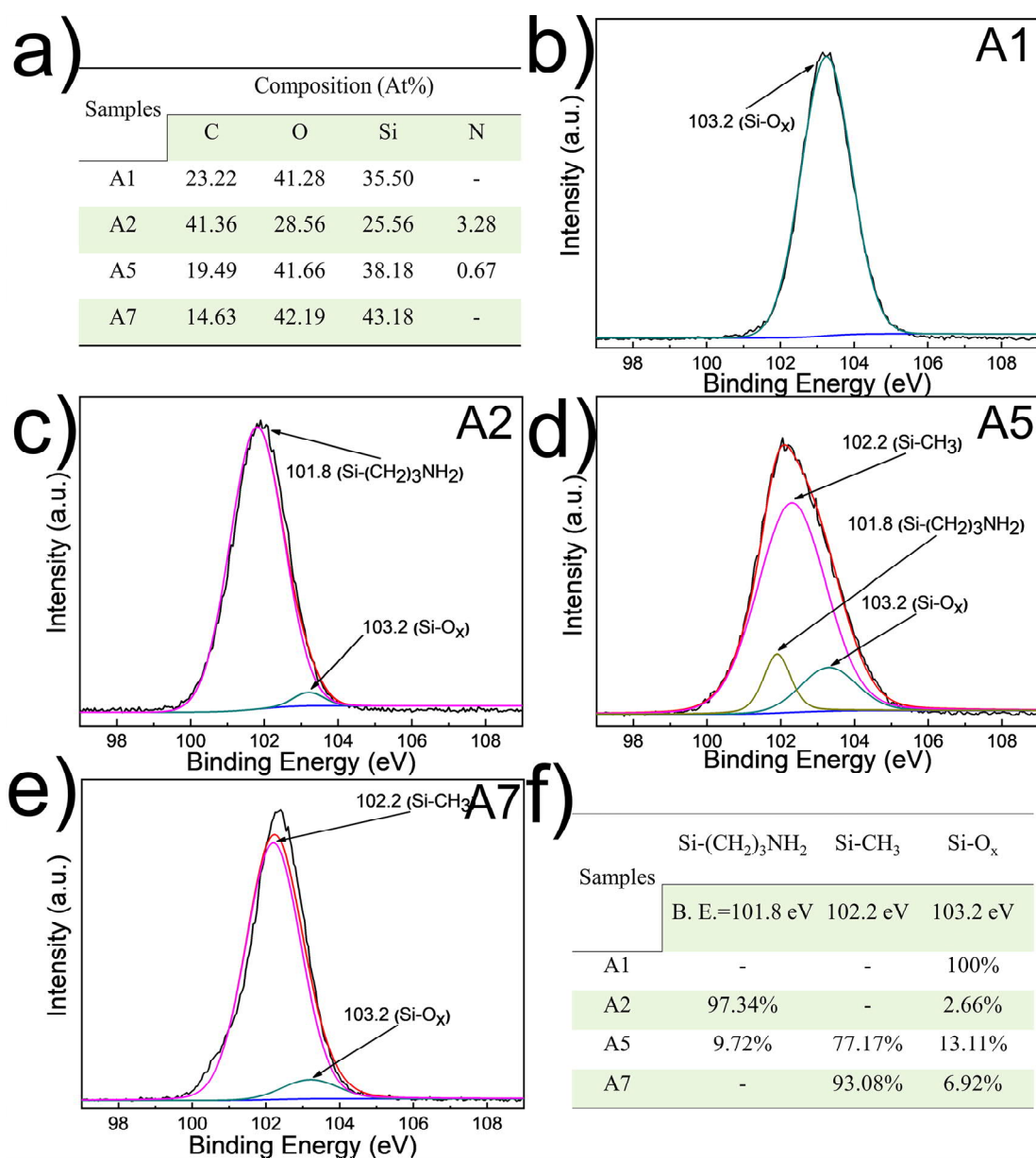


Fig. S5 X-ray photoelectron spectroscopy (XPS) analyses of the SiO₂ particles: (a) Atomic composition summary of samples A1, A2, A5, and A7 shown in Fig. 2c. Peak fittings and identifications of Si-related patterns in (b) A1, (c) A2, (d) A5, and (e) A7, respectively; (f) the summary of the results from (b)-(e). The integrated features of A5 from A2 and A7 verify a successful grafting of APTES and DCDMS.

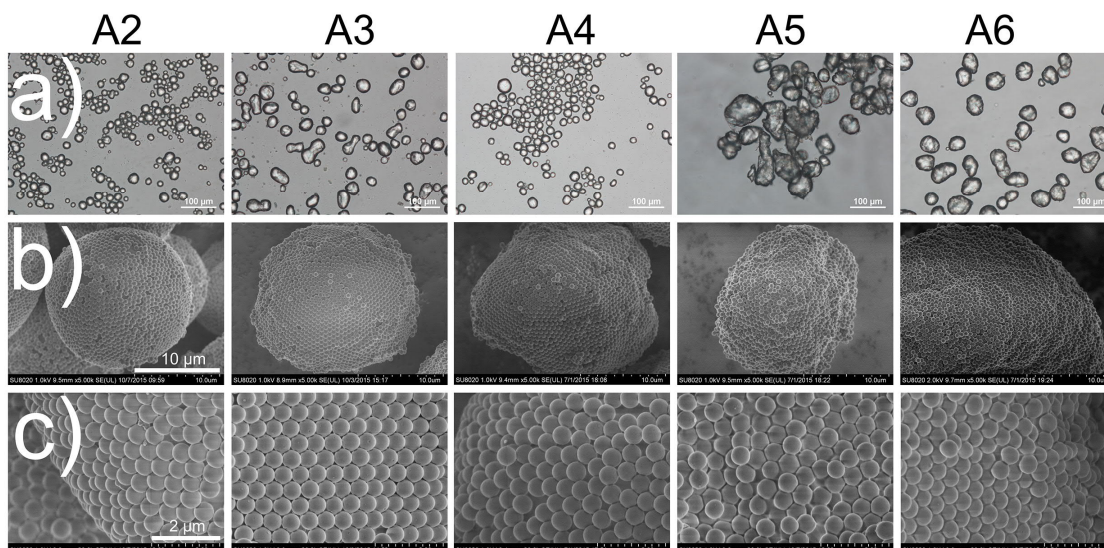


Fig. S6 The SEM and optical microscopy observation of Pickering emulsions stabilized with SiO₂ particles: images of samples A2-A6 correspond to the images shown in Fig. 2d. The concentration ratios of APTES and DCDMS (C_{APTES}/C_{CMDCS}) used for A2-A6 are detailed in Table 1 and Table S1. Optical microscopic overviews (a) of wax-in-oil Pickering emulsions. SEM images (b) focus on the single emulsion droplet, and (c) local details of each samples. SiO₂ particles treated with APTES and DCDMS in the C_{APTES}/C_{CMDCS} range of 1:0 to about 1:0.636 are capable of stabilizing wax-in-oil Pickering emulsions.

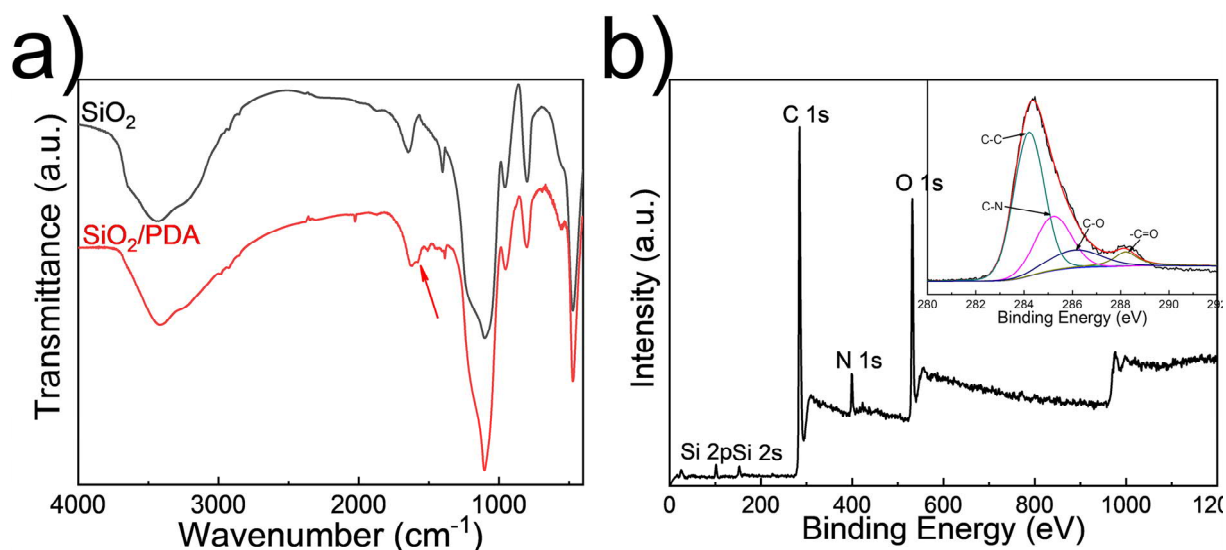


Fig. S7 Characterization of SiO₂/PDA Janus particles: (a) FTIR comparison of SiO₂ particles (A5) before and after surface modification with PDA. The new weak peak appeared at 1580 cm⁻¹ pointed by the red arrow. This is assigned to a bending vibration of the N-H bond, which is present in the PDA structure;² (b) XPS results of SiO₂/PDA Janus particles. The inset is the peak identification of the C 1s pattern. Comparing with the XPS spectrum of sample A5 shown in Fig. 2c, the intensity of the N1s is more pronounced in that of SiO₂/PDA Janus particles, hinting the surface coating of SiO₂ with PDA.

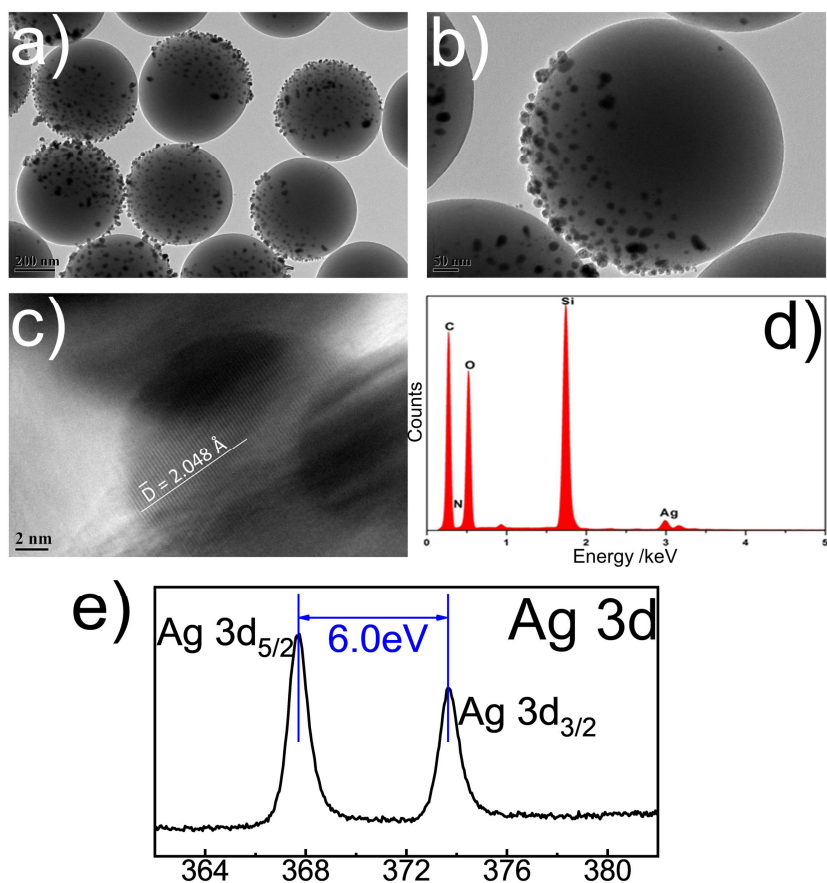


Fig. S8 TEM, energy-dispersive X-ray spectroscopy (EDX), and XPS characterization of $\text{SiO}_2/\text{PDA-Ag}$ Janus particles. TEM images show (a) the overview of and (b) individual $\text{SiO}_2/\text{PDA-Ag}$ Janus particles, and the magnified view (c) of Ag nanoparticles on the surfaces of the Janus particles. The lattice space shown in c) corresponds to the (200) plane of Ag, confirming the formation of Ag nanoparticles. d) EDX analysis of $\text{SiO}_2/\text{PDA-Ag}$ Janus particles. These results are strong evidence for the formation of $\text{SiO}_2/\text{PDA-Ag}$ Janus particles, which are consistent with the results shown in Fig. 3a and b. e) XPS analysis of Ag shown in Figure 3b-iv.

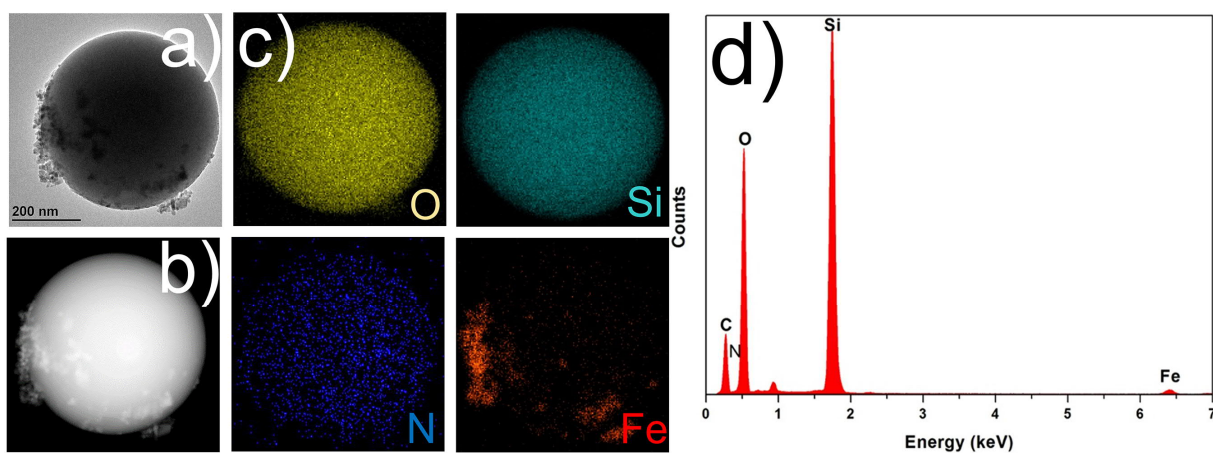


Fig. S9 Characterization of $\text{SiO}_2/\text{PDA-Fe}_3\text{O}_4$ Janus particles: (a) TEM, (b) dark field TEM, (c) elemental mapping, and (d) EDX analyses of $\text{SiO}_2/\text{PDA-Fe}_3\text{O}_4$ Janus particles. The combination of these results with those shown in Fig. 3c confirms the formation and Janus structure of $\text{SiO}_2/\text{PDA-Fe}_3\text{O}_4$ Janus particles.

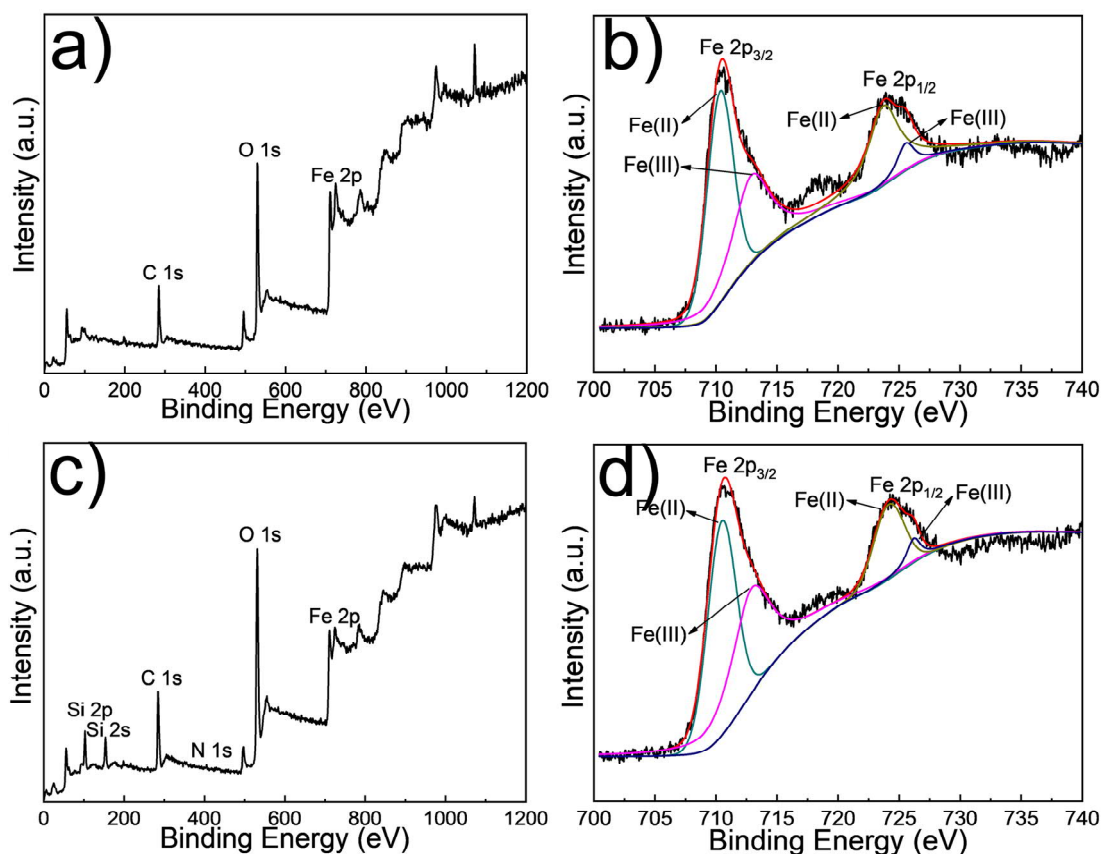


Fig. S10 XPS analyses of Fe_3O_4 nanoparticles that are stabilized with trisodium citrate (a) and (b), and $\text{SiO}_2/\text{PDA}-\text{Fe}_3\text{O}_4$ Janus particles (c) and (d), respectively. New Si and N characteristic peaks emerge as comparing to the spectra shown (a) and (c), which belong to SiO_2/PDA Janus particles. This verifies the successful grafting of Fe_3O_4 nanoparticles onto SiO_2/PDA Janus particles, resulting in $\text{SiO}_2/\text{PDA}-\text{Fe}_3\text{O}_4$ Janus particles. The results shown in (b) and (d) demonstrate that the composition of the Fe_3O_4 nanoparticles retain regardless of the grafting, which agrees well with the results of the magnetic property measurement shown in Fig. 3c-iv.

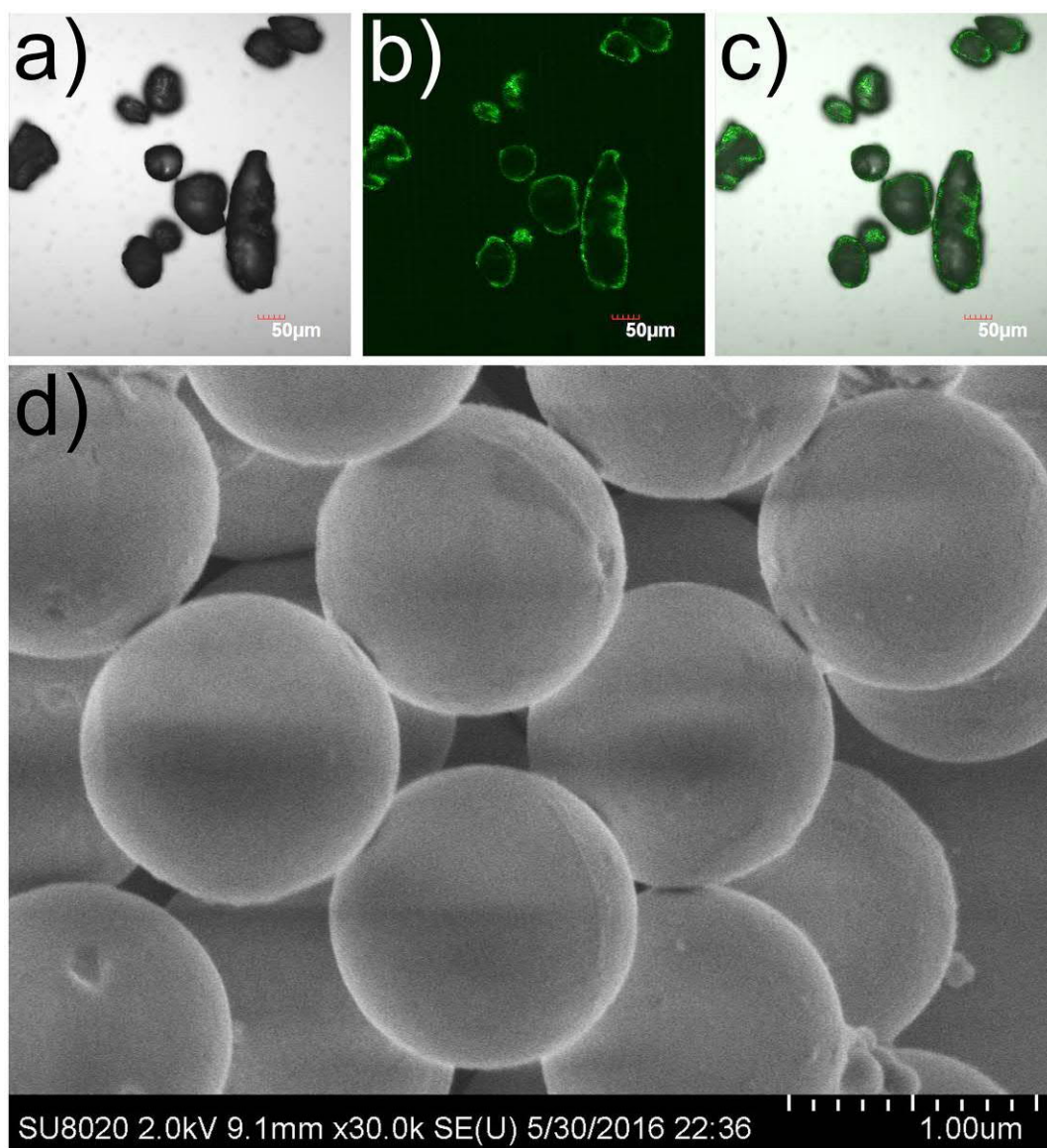


Fig. S11 Characterization of SiO₂/PDA-FITC Janus particles: optical (a), confocal laser scanning microscopy (b), and their integrated micrographs of Pickering emulsions stabilized by SiO₂/PDA-FITC Janus particles; SEM image d) of SiO₂/PDA-FITC Janus particles, which corresponds to samples shown in Fig. 3d.

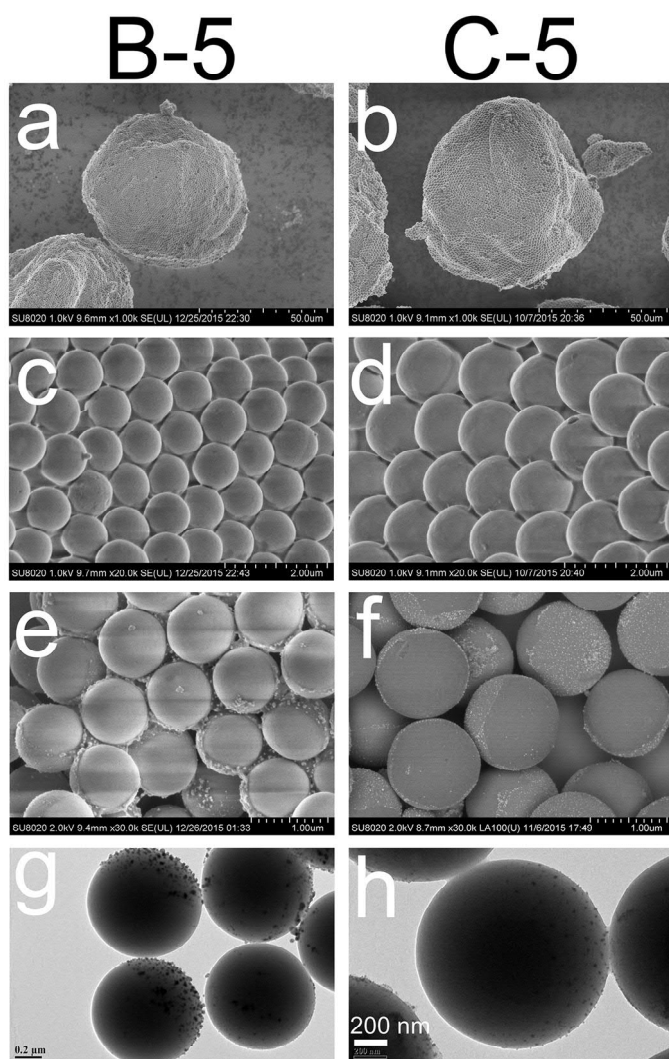


Fig. S12 Preparation of SiO₂/PDA-Ag Janus particles from larger SiO₂ matrix particles: SiO₂ particles batch B (mean diameter = 0.88 μm and polydispersity = 2.8%) and C (mean diameter = 1.25 μm and polydispersity = 1.7%) as shown in Fig. S1 are used as the matrixes; SEM images of the wax droplets stabilized with particles batch B (a) and C (b), magnified local details of the wax surfaces (c) and (d), SiO₂/PDA Janus particles: B-5/PDA (e) and C-5/PDA (f), and SiO₂/PDA-Ag Janus particles: B-5/PDA-Ag (g) and C-5/PDA-Ag (h). Note that the recipes used to modify the surfaces of big SiO₂ matrix particles batch B and C are the same to that used for batch A-5 in Table S1. These results reveal that our method is a general route towards Janus particles regardless of the size of the SiO₂ colloidal matrix particles employed.

3. Supplementary References

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