

Supporting Information for:

**An efficient and reusable “hairy” particle acid catalyst for the
synthesis of 5-hydroxymethylfurfural from dehydration of fructose
in water**

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Experimental Section

Materials. Tetraethyl orthosilicate (98%), ammonium hydroxide (25% in water), and triethoxysilane (95%) were purchased from Acros Organics and used as received. Platinum-divinyltetramethyldisiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) was obtained from Gelest, Inc. CuCl (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and ethyl ether. The purified CuCl was then collected, dried under vacuum, and stored in a desiccator. *N, N, N', N', N''*-Pentamethyldiethylenetriamine (99 %, Aldrich) was dried with calcium hydride, distilled under a reduced pressure, and stored in a desiccator. D-(-)-Fructose (> 99%) and 5-hydroxymethylfurfural (analytical standard) were purchased from Aldrich. All other chemical reagents were obtained from either Aldrich or Fisher and used without further purification.

General Characterization. ¹H NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. The particle samples for TGA were dried at 45 °C in vacuum for at least 5 h. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) experiments were conducted on a HITACH HD2000 microscope with an accelerating voltage of 200kV. Fourier transform infrared (FTIR) spectroscopy experiments were performed on a Perkin Elmer Frontier FTIR spectrometer equipped with a diamond attenuated total reflectance (ATR) attachment and the spectra were recorded over the range of 600-4000 cm⁻¹. The yields of 5-hydroxymethylfurfural (HMF) in the fructose dehydration reactions were determined using a HPLC system (ShimadzuCBM-10AW VP) equipped with a UV-vis detector and a C18 column (250 mm × 4.6 mm, particle size: 5 μm). The mobile phase was water (HPLC grade) at a flow rate of 1.0 mL/min and the detection

wavelength was 300 nm. Prior to the measurements, the samples were diluted with water (HPLC grade). The conversion of fructose was determined by the phenol-sulfuric acid method.¹ A mixture containing 0.1 mL of the reaction sample (the water-soluble portion), 0.9 mL of deionized water, 1 mL of 5% phenol (freshly distilled) and 5 mL of 98% concentrated sulfuric acid was prepared. The analysis was performed on an Evolution 600 UV-vis spectrophotometer at about 490 nm. The concentration of fructose in the reaction mixture was calculated based on the standard curve obtained with fructose.

Synthesis of Bare Silica Particles. Ammonium hydroxide (25% in water, 19.901 g) and tetraethyl orthosilicate (TEOS, 10.512 g) were each mixed with 10 mL of ethanol. The two solutions were then added into a 500 mL one-necked flask that contained 280 mL of ethanol under the stirring condition. The concentrations of NH₃, TEOS, and water in the solution were 0.61 M, 0.22 M, 3.56 M, respectively. The mixture was stirred vigorously at room temperature overnight. The silica particles were isolated by centrifugation (Eppendorf 5804 centrifuge, 8000 rpm), redispersed in ethanol, and centrifugated again. This washing process was repeated with ethanol additional two times, water two times, and ethanol again. The particles were then dried with a stream of air flow (yield: 3.20 g). The average diameter of silica particles, measured by TEM, was 175 nm.

Immobilization of an ATRP Initiator on the Surface of Silica Particles. The ATRP initiator-functionalized silica particles (initiator particles) were prepared by the immobilization of 2-[4-(chloromethyl)phenyl]ethyltriethoxysilane onto the surface of bare silica particles via an ammonia-catalyzed hydrolysis and condensation process.² The details are described below.

4-Vinylbenzyl chloride (812.2 mg, 5.322mmol) was weighed into a 25 mL two-necked flask, followed by the injection of triethoxysilane (3.0 mL, 27.5 mmol) and the Pt complex in xylene

(75 μ L). The mixture was stirred at 45 °C under the nitrogen atmosphere, and the hydrosilylation reaction was monitored by ^1H NMR spectroscopy analysis. Once the reaction was complete, excess triethoxysilane was removed under high vacuum at 45°C. The product, 2-[4-(chloromethyl)phenyl]ethyltriethoxysilane, was purified by column chromatography using dichloromethane as solvent. Yield: 0.57 g (66.0 %). ^1H NMR (CDCl_3) δ (ppm): 1.22 (9H, - OCH_2CH_3), 3.81 (6H, - OCH_2CH_3), 0.96 (2H, - SiCH_2CH_2 -), 2.71 (2H, - SiCH_2CH_2 -), 7.26 (4H, - C_6H_4 -) and 4.54 (2H, - CH_2Cl). ^{13}C NMR (CDCl_3) δ (ppm): 145.2, 135.0, 128.8, 128.4, 58.6, 46.4, 28.8, 18.5, 12.6.

Bare silica particles (511.6 mg) were dispersed in a mixed solvent of ethanol (35.0 mL) and THF (35.0 mL) by ultrasonication to form a homogenous, stable dispersion. A solution of ammonium (25% in water, 5.0118 g) in a mixture of ethanol (10.0 mL) and THF (10.0 mL) was added dropwise into the particle dispersion. After the reaction mixture was stirred at 40 °C for 2 h, a solution of freshly synthesized 2-[4-(chloromethyl)phenyl]ethyltriethoxysilane (350.0 mg) in dry THF (5.0 mL) was added dropwise into the dispersion. The mixture was then stirred at 40 °C for 18 h. The particles were separated by centrifugation and re-dispersed in THF. This process was repeated for a total of five times. The obtained ATRP-initiator-functionalized silica particles were dried with a stream of N_2 flow.

Synthesis of Poly(4-styrenesulfonic acid) Brush-Grafted Silica Particles. The initiator particles (421.5 mg) were dispersed in a mixture of methanol (9.992 g) and water (35.003 g) in a 100 mL three-necked flask by ultrasonication to form a dispersion. CuCl (16.8 mg, 0.170 mmol), sodium 4-styrenesulfonate (10.413 g, 50.5 mmol), and benzyl chloride (20.7 mg, 0.164 mmol) were then added into the flask and stirred under a N_2 atmosphere. After the mixture was degassed by three freeze-pump-thaw cycles, N,N,N',N',N'' -pentamethyldiethylenetriamine (29.8 mg, 0.170

mmol) was injected into the solution using a degassed microsyringe. The flask was then placed into a 75 °C oil bath, and the polymerization was monitored by ¹H NMR spectroscopy analysis. After the monomer conversion reached 100 % (at ~ 5.7 h), the flask was removed from the oil bath and opened to air. H₂O (~10 mL) was added into the flask to dilute the mixture. The particles were isolated by centrifugation, redispersed in an HCl aqueous solution with pH of ~1, and centrifuged again. This washing process was repeated with acidic water additional five times, followed by drying of the hairy particles under high vacuum at 50 °C overnight. The free polymer formed from the free initiator, benzyl chloride, was purified by dialysis against a HCl aqueous solution (pH = ~ 1) for 3 days using a regenerated cellulose tubular dialysis membrane with a nominal MWCO of 3500. The HCl aqueous solution with pH of ~ 1 was changed every 2 h in the first two days and then twice in the third day. The water was then rotavapored at 80 °C, and the obtained free polymer was then dried at 50 °C under high vacuum overnight. The degree of polymerization of the free polymer was 309, calculated by using the monomer conversion and the monomer-to-initiator ratio.

Calculation of Polymer Content and Grafting Density of Poly(4-styrenesulfonic acid) (PSSH) Brush-Grafted Silica Particles. We assume that $m_{ip}(800\text{ °C}) = m_{hp}(800\text{ °C})$, where m_{ip} and m_{hp} represent the masses of a single initiator particle and a single hairy particle, respectively, at 800 °C in TGA analysis.^{3,4} The weight retentions of the initiator particles at 100 and 800 °C are 94.05% and 86.44%, respectively, while the weight retentions of the PSSH hairy particles at 100 and 800 °C are 99.57% and 58.30%, respectively. We believe that the difference in the weight retentions of initiator particles and PSSH hairy particles at 100 °C is caused by the different amounts of absorbed water. To correct this difference, we vertically shifted the TGA curve of initiator particles upward such that the weight retentions of both initiator and hairy

particles at 100 °C are the same (i.e., 99.57%). Thus, the corrected weight retention of initiator particles at 800 °C is 91.96 % (99.57% - 94.05% + 86.44% = 91.96%). We calculated the mass ratios of the volatile portion to the silica residue at 800 °C for initiator particles and PSSH hairy particles and they are 8.74 : 100, and 71.53 : 100, respectively. Therefore, the ratio of the amount of the grafted PSSH polymer to the silica residue at 800 °C is 62.79 : 100. The polymer content in the hairy particles is $62.79/(71.53 + 100) = 36.6$ wt %.

Assuming that the silica particles are spherical and the density is 2.07 g/cm^3 ,³⁻⁵ a calculation shows that the mass of a single silica particle with a diameter of 175 nm is 5.81×10^{-15} g. Therefore, the amount of the grafted PSSH in one hairy particle is 3.65×10^{-15} g. The actual molecular weight of PSSH is $309 \times 183 \text{ g/mol} = 56547 \text{ g/mol}$. Thus, the number of grafted polymer chains in one hairy particle is $(3.65 \times 10^{-15} \text{ g}/56547 \text{ g/mol}) \times 6.022 \times 10^{23} = 3.89 \times 10^4$ chains. The surface area of one bare silica particle is $\pi D^2 = 9.62 \times 10^4 \text{ nm}^2$. Therefore, the grafting density of PSSH brushes on silica particles is 0.40 chains/nm².

Dehydration of Fructose Using Poly(4-styrenesulfonic acid) Brush-Grafted Silica Particles as Catalyst. Poly(4-styrenesulfonic acid) brush-grafted silica particles (0.10 g), fructose (0.23 g), and deionized water (3.5 mL) were added into a 25 mL round-bottom flask. The reaction mixture was stirred with a magnetic stirrer in a 120 °C oil bath. N₂ was used for purging air inside the reactor and keeping a certain pressure to prevent boiling. After the reaction proceeded for a predetermined amount of time (3, 6, 10 or 20 h), the flask was removed from the oil bath, and the reaction mixture was centrifugated (Eppendorf 5804, 8500 rpm, 30 min). The supernatant liquid was analyzed by HPLC based on the standard curve obtained with pure HMF (external standard method). The particles were washed with deionized water once first and then a HCl aqueous solution (pH = ~ 1) five times to remove any byproducts. The hairy particles were

dried at 50 °C under high vacuum overnight. For recycling experiments, the reaction time for the dehydration of fructose was set at 6 h. The hairy particles were reused, and the yield of HMF in each round of experiment was measured by HPLC.

Dehydration of Fructose Using Free Poly(4-styrenesulfonic acid) as Catalyst. The dried free polymer poly(4-styrenesulfonic acid) (0.0366 g), fructose (0.23 g), and deionized water (3.5 mL) were added into a 25 mL round-bottom flask. The reaction mixture was stirred in a 120 °C oil bath. After a certain amount of time (3, 6, 10 or 20 h), the flask was removed from the oil bath, and the reaction mixture was passed through a basic alumina column to remove the polymer catalyst. The eluent was then analyzed by HPLC based on the standard curved made with HMF (external standard method).

Estimation of Yields of Levulinic Acid in the Hairy Particle-Catalyzed Dehydration of Fructose to HMF. It is known that HMF can be further hydrated to form levulinic acid in the acid-catalyzed dehydration of fructose. Interestingly, we found that that the reaction time had little effect on the HMF selectivity in our hairy particle catalyst system as shown in Figure 2, which indicated that the further hydration reaction of HMF was restrained. To confirm this, we need to determine how the yield of levulinic acid changed with the reaction time. However, the yield of levulinic acid cannot be determined by the same HPLC setup used to measure the yield of HMF. Therefore, we used mass spectrometry to estimate the yields of levulinic acid at reaction times of 3, 6, 10, and 20 h in the experiment for Figure 2a based on the yields of HMF through a semi-quantitative method. Since the yields of HMF were known from HPLC, we used HMF, observed at m/z 127 in positive-ion mode in mass spectrum, as the internal standard to estimate the yield of levulinic acid (observed at m/z 117 in positive-ion mode) in the same reaction mixture. Mass spectrometry was performed using a JEOL (Peabody, MA, USA)

orthogonal time-of-flight (TOF) mass spectrometer (model JMS-T100LC) with an IonSense (Danvers, MA, USA) direct analysis in real time (DART) source in positive-ion mode. Helium gas was used for the DART source at a flow rate of 4 L/min and heated to be 300 °C. The mass acquisition range was m/z 100-300 with spectra recording interval of 0.1 s. Five standards were prepared in aqueous solutions with the concentration ratio of levulinic acid to HMF ranging from 0 %, to 23 %, to 30 %, to 55 %, and 83 % and the concentration of HMF being held at 2.5 %. Each standard was examined by DART-TOFMS five times. The average intensity ratio of ions at m/z 117 (levulinic acid) to m/z 127(HMF) was plotted against the concentration ratio of levulinic acid to HMF. As shown in Figure S3, a nearly linear relationship was observed with R of 0.9959, suggesting that it is feasible to use the mass spectrometry to estimate the yields of levulinic acid on the basis of the yields of HMF. A linear equation $Y=0.2756X-0.0048$ was obtained from the plot. The mass spectra of the reaction mixtures taken at 3, 6, 10, and 20 h were analyzed by mass spectrometry in the same manner. Figure S4 shows a mass spectrum of the reaction mixture at a reaction time of 20 h. The peaks of $[\text{HMF} + \text{H}]^+$ and $[\text{levulinic acid} + \text{H}]^+$ can be clearly seen. Based on the yields of HMF at four different reaction times determined by HPLC, the relative yields of levulinic acid in the reaction mixtures were calculated using the calibration curve and are shown in Figure S5. Clearly, the yield of levulinic acid did not change much after 6 h, suggesting that the further hydration of HMF was indeed restrained.

References:

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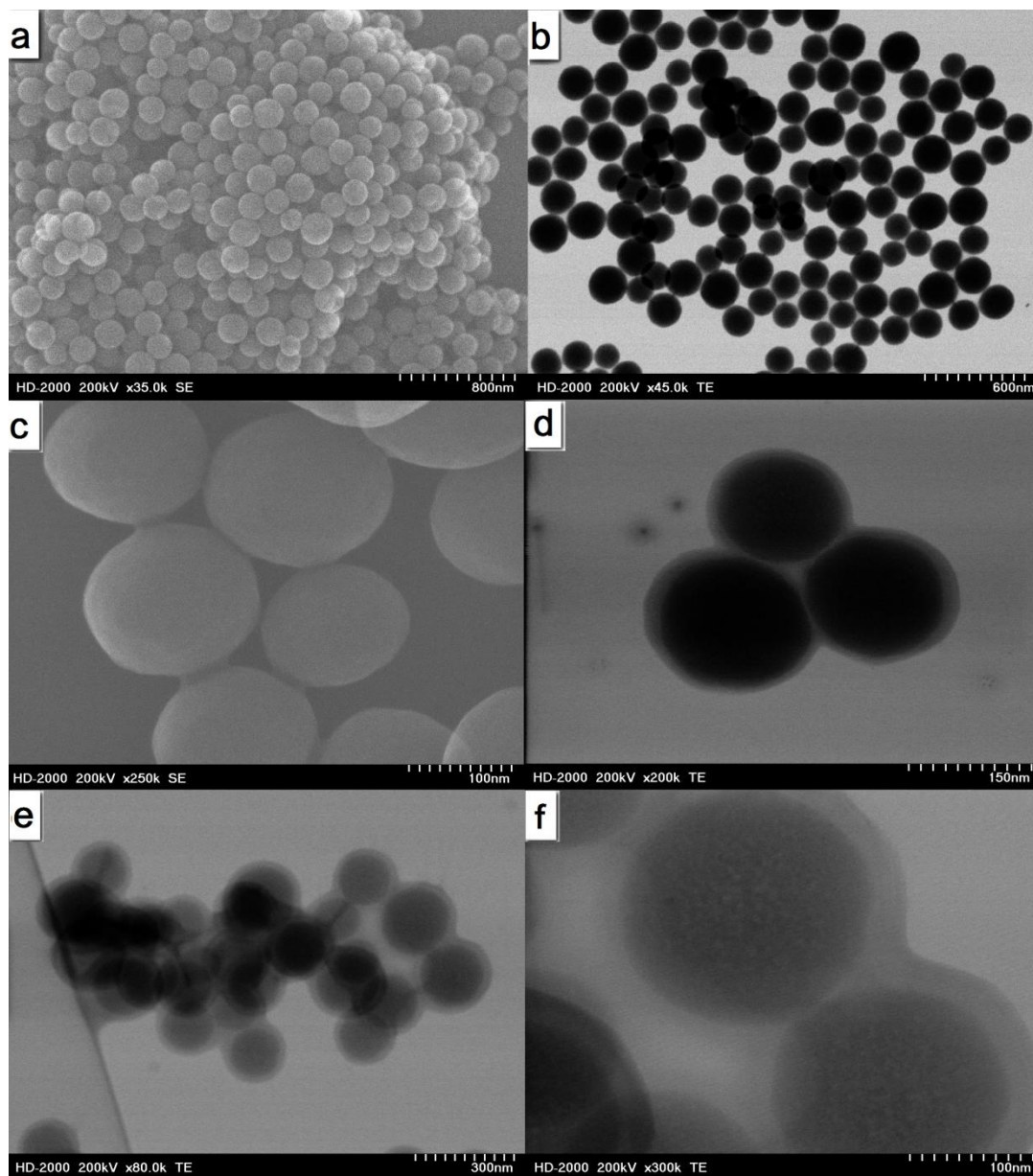


Figure S1. Scanning electron microscopy (SEM) images of bare silica particles (a) and ATRP-initiator-functionalized silica particles (c), and transmission electron microscopy (TEM) images of bare silica particles (b), ATRP-initiator-functionalized silica particles (d), and poly(4-styrenesulfonic acid) brush-grafted silica particles (e and f).

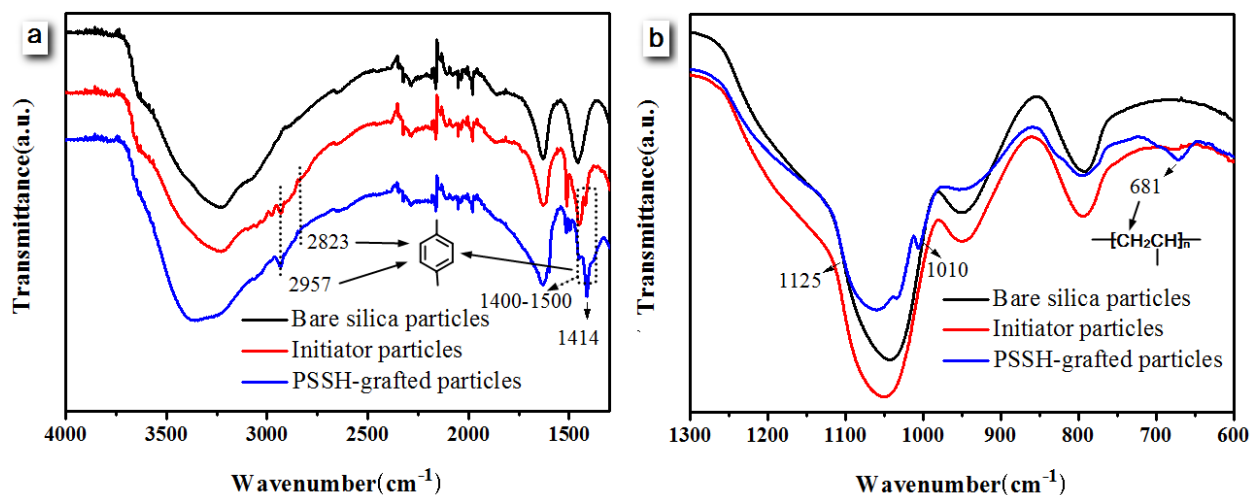


Figure S2. FTIR spectra of bare silica particles, initiator particles, and poly(4-styrenesulfonic acid) brush-grafted silica particles in the range of (a) 1300-4000 cm⁻¹ and (b) 600-1300 cm⁻¹.

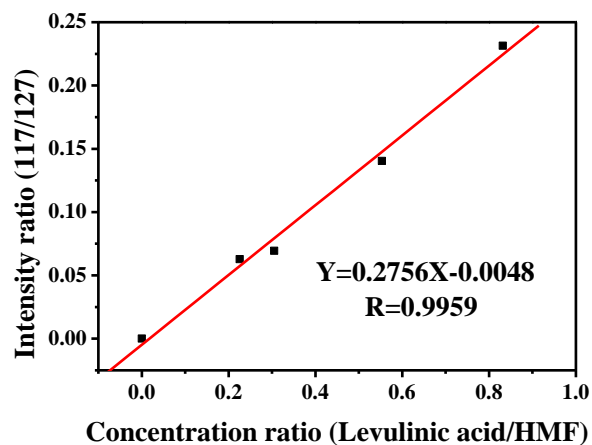


Figure S3. The standard curve established by plotting the average intensity ratio of ions at m/z 117 over m/z 127 against concentration ratio of levulinic acid over HMF.

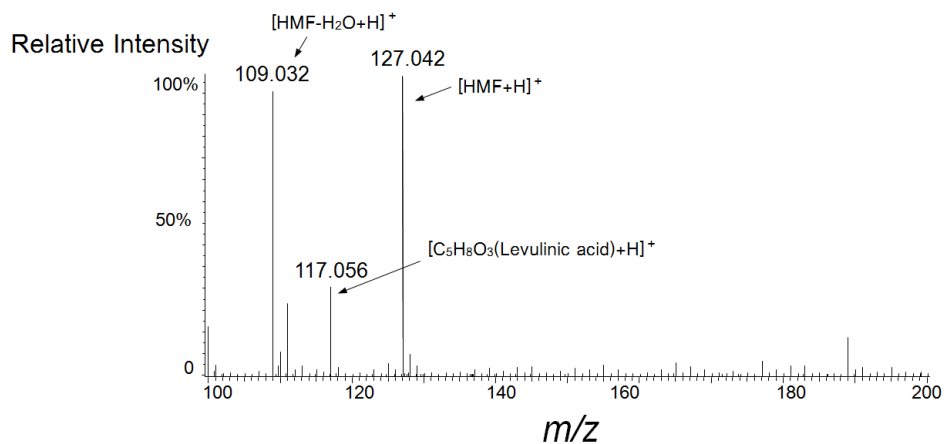


Figure S4. Mass spectrum of the quenched reaction mixture at 20 h from the experiment of hairy particle-catalyzed dehydration of fructose using DART-TOFMS in the positive-ion mode calibrated with external standards (PEG200).

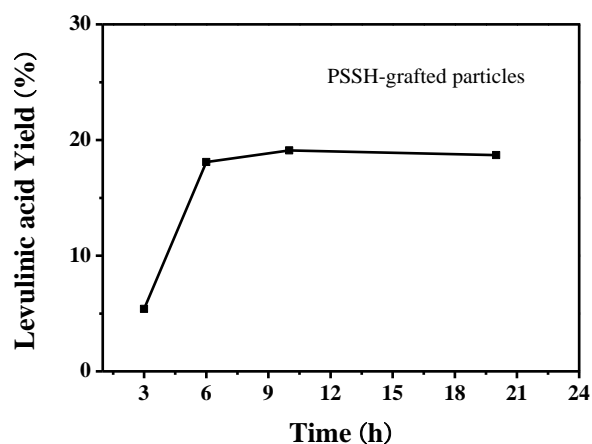


Figure S5. Effect of reaction time on the yield of Levulinic acid in the hairy particle-catalyzed dehydration of fructose to HMF.