Supporting Information

Effect of (3-Aminopropyl)triethoxysilane on dissolution of silica nanoparticles synthesized via reverse micro emulsion

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Fig S1. Descriptions of the five different silica nanoparticle preparations performed via reverse micro emulsion. The procedures in the figure describe the addition order of each chemical and base after the microemulsion was formed. For all procedures, after the final 24 hours of condensation, the washing step described in the Experimental and Method section was performed. The molar ratio of TEOS to APS was 30.



Fig S2. Representative TEM images of the nanoparticles prepared as described in Fig S1. The letter designation on each TEM image matches the nanoparticle preparation route shown in Figure S1.



Fig S3. The diameter distributions measured from TEM images for the nanoparticles prepared as described in Fig S1. The letter designations are consistent with those shown in Fig S1 and S2. Statistical significance testing was performed via one-way ANOVA with Tukey's multiple

comparisons test to see the diameter difference between particle A and the rest: **p<0.01 and ****p<0.0001. At least 200 nanoparticles were measured per sample type.



Fig S4. TEM images of the two nanoparticles prepared with the molar ratio of TEOS to APS of 1, before and after dissolution in water (for 24 hours at 0.1 mg/mL). a) The nanoparticles synthesized with procedure D in Fig S1. b) The nanoparticles synthesized with procedure E in Fig S1.



Fig S5. The diameter distributions measured from TEM images for the nanoparticles prepared with procedure D in Fig S1 (APS:TEOS = 1:1 molar ratio) before and after aqueous aging, as show in Fig S4a. The red line represents the average. Statistical significance testing was performed via one-way ANOVA with Tukey's multiple comparisons test to evaluate diameter change after dissolution, ****p < 0.0001.



Fig S6. Solid-state²⁹ Si silicon NMR spectra from (TEOS+APS)_{core} (a) pre and (b) post aging. Each sample is analyzed via both Bloch-Decay (BD) method (green) and the cross-polarization (CP) method (maroon). Q4: silicon fully condensed, Q3: silicon from TEOS with triple siloxane bond, Q2: silicon from TEOS with double siloxane bonds, and T: silicon from APS. BD-NMR is a traditional way to obtain the actual silicon molecular state and amount, and CP-NMR uses the polarization from proton nuceli to improve the NMR signal of the silicon near proton.¹ As a result, much clearer peaks from APS silicon were obtained.

1. Kolodziejski W, Klinowski J. Kinetics of Cross-Polarization in Solid-State NMR: A Guide for Chemists. Chem Rev. 2002 Mar 1;102(3):613–28.



Fig S7. Proposed APS-catalyzed siloxane bond hydrolysis mechanism.



Fig S8. TEM images of nanoparticles before and after incubation in water for 5 days, prepared as described for $(TEOS+APS)_{core}(APS)_{shell}$, but with varied shell functionalization. For the shell part, instead of APS, the first three nanoparticles, from left to right, were functionalized with TEOS, TMS, and PEG during preparation. Each nanoparticle was suspended at a concentration of 0.1 mg/mL. The TEM images in the top row show the nanoparticle prior to dissolution, and the images in the second bottom row show the nanoparticle after dissolution.



Fig S9. TEM images of nanoparticles after incubation in water for 5 days. In these, the pH was adjusted with NH_4OH at 11.4 before the nanoparticles were suspended.



Fig. S10. Normalized mobility distribution functions of (TEOS)_{core}(APS)_{shell}, (TEOS+APS)_{core}, and (TEOS+APS)_{core}(APS)_{shell} nanostructures.