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One-step Synthesis of Water Dispersible Silica Nanoplates

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Experimental Section

Materials. All reagents were obtained from commercial sources and without further purification. Tetrahydrofuran (THF) and hexane were dried by purging with nitrogen and passing through alumina columns prior to use. *N*,*N*'-dimethylformamide (DMF) was treated with free amine scavenger (Aldrich) before passed through 4Å molecular sieves and activated alumina column. Tandem size exclusion chromatography/laser light scattering (SEC/LLS) was done at 60 °C using an SSI pump connected to Wyatt Optilab DSP and Wyatt DAWN EOS light scattering detectors. Separations were achieved using 10^5, 10^4, and 10^3 Å Phenomenex Phenogel 5 μm columns with 0.1 M LiBr in DMF as eluent and polypeptide concentrations of about 10 mg/mL. Millipore water was obtained from a Millipore Milli-Q Biocel A10 purification unit. α-amine-ε-monomethyl poly(ethylene glycol) with Mn=2000 Da was purchased from Aldrich. Their polydispersity index is below 1.2.

Characterization: For SEM measurements, the dried samples were placed on a double-sided sticky carbon tape mounted on aluminum sample holders and then sputter coated with platinum for SEM analysis. They were then investigated using a JEOL-6700 field-emission scanning electron microscope. Transmission electron microscopy (TEM) samples were examined on a JEM2200FS microscope operated at 200 kV. TEM samples were prepared by casting sample solution on carbon coated TEM grids. For Dynamic Light Scattering (DLS) measurements, the dried samples were dispersed in different solvents under stirring. The size of silica nanoplates was characterized using particle analyzer Zetasizer Nano ZS at 25 °C.

The particle size distribution was analyzed using DTS Software (V5.0).

Experimental Section

Synthesis of Poly(ethylene glycol)-b-poly-L-lysine. Nε-carbobenzyloxy-L-lysine-N-carboxyanhydride (Z-Lys-NCA) was synthesized using triphosgene solution in THF described before.[21] Poly(ethylene glycol)-*b*-poly-L-lysine (PEG-PLL) diblock copolymers were prepared via PEG-NH_2 initiated ring-opening polymerization (ROP) of Z-Lys-NCA in DMF. Typically, a desired amount of Z-Lys-NCA/THF solution (50 mg/mL) was added to PEG-NH_2/DMF solution, and the solution was stirred three days prior to SEC/LLS measurements. The number averaged molecular weight of PZLL block was calculated given known PEG molecular weight from ^{1}H NMR spectrum. The molecular weight distribution of PEG-PZLL was narrow with PDI ranging between 1.1 and 1.3. After polymerization, the crude products were dried and re-dissolved in trifluoroacetic acid. The CBZ groups were removed with excess HBr (33 wt% in acetic acid) at 0 °C, and the products were precipitated into excess diethyl ether. The obtained solid products were then dispersed in deionized water and transferred to a dialysis bag. The solutions were dialysized against HCl solution (pH ~ 3) for two days with water changed every 12 hours. Then, the solutions were dialyzed against deionized water for another 3 days with the water changed every 12 hours before the solution was lyophilized to obtain the dried samples.

Preparation of Silica Nanoplates. Tetramethoxysilane (300 μL) in HCl (1 mM, 1.7mL) was incubated for 5 minutes at room temperature to provide monosilicic/oligosilicic acid precursors. Generally, PEG-PLL diblock copolymer solution (10 mg/mL) was mixed with phosphate buffer (0.1 M) prior to the addition of silicic acid precursor solutions. The molar ratio of phosphate and lysine residue and the mole ratio between silicic acid and lysine residue were changed to study phosphate and silicic acid concentration effects. Typically, 10 μL of PEG_{45}-PLL_{100} solution (10 mg/mL) was also dispersed in 20 μL of sodium phosphate buffer (pH 7.5, 0.1 M) with the ratio of [phosphate]/[NH_3^+]=5 for about 5 minutes. Then a freshly prepared solution of monosilicic acid (1.0 M, 10 μL) was added to the above mixture in centrifugal tube under votex agitaion. The reaction medium turned into cloudy within a few minutes. The products were then isolated via centrifuge to give white solid subject to structure characterization.

Additional Results

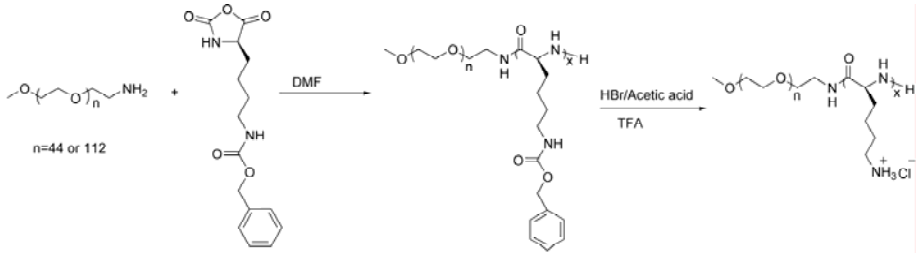

Fig. S1 Synthetic routes to PEG-PLL diblock copolymers.

Table S1 Molecular parameters of PEG-PLL diblock copolymers.

Samples	[a]PDI	[b]DP of PLL block
PEG_{45}-PLL_{15}	1.6	15
PEG_{45}-PLL_{45}	1.2	45
PEG_{45}-PLL_{100}	1.1	100
PEG_{45}-PLL_{140}	1.1	140

[a]Polydispersity index determined by SEC/LLS, [b]Molecular weight determined by ^1H NMR.

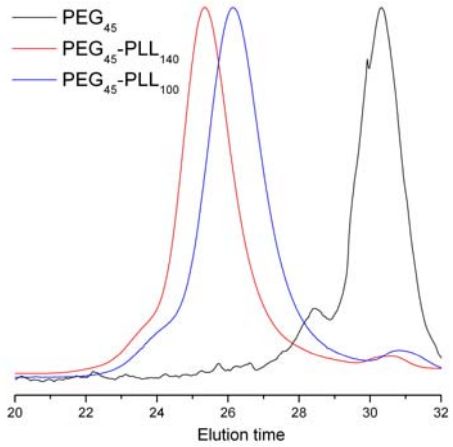

Fig. S2 GPC traces of $mPEG_{45}$-NH_2 and PEG_{45}-PLL_{100}, and PEG_{45}-PLL_{140} diblock copolymers.

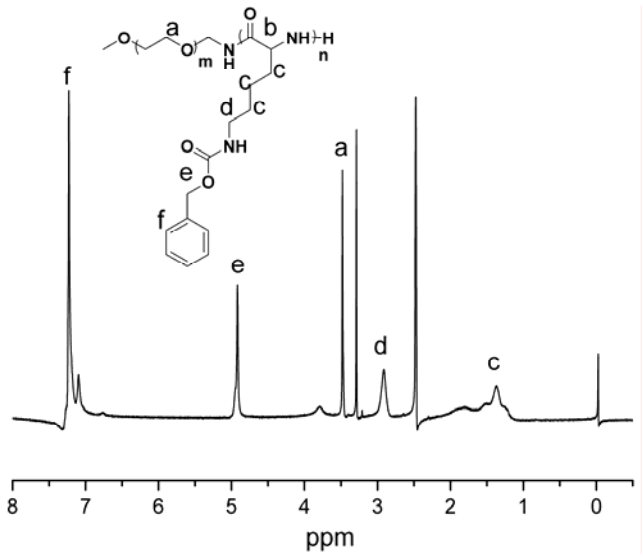

Fig. S3 ^{1}H NMR spectrum of a PEG_{45}-PLL_{100} diblock copolymer.

Fig. S4 Optical photos of isolated silica nanoplates re-dispersed in water (left) and $CHCl_3$ (right).

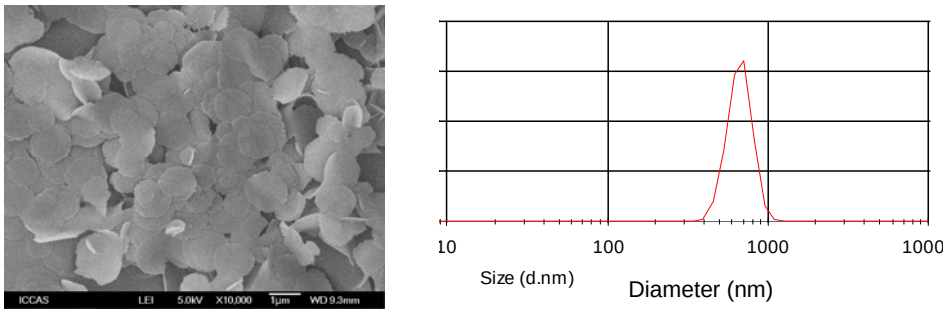

Fig. S5 Silica nanoplates directed by PEG_{45}-PLL_{100} (Left) and corresponding size distribution in water (Right).

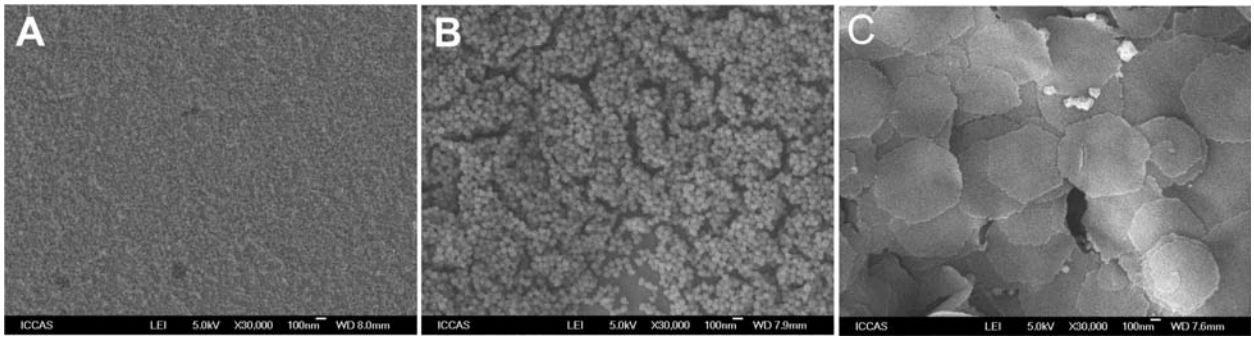

Fig. S6 Effects of phosphate concentration on resulting silica morphology. SEM images of silica templated by PEG_{45}-PLL_{100} (c=10 mg/mL) under conditions of (**A**) [phosphate]/[NH_3^+]=0.5, (**B**) [phosphate]/[NH_3^+]=1, (**C**) [phosphate]/[NH_3^+]=5.

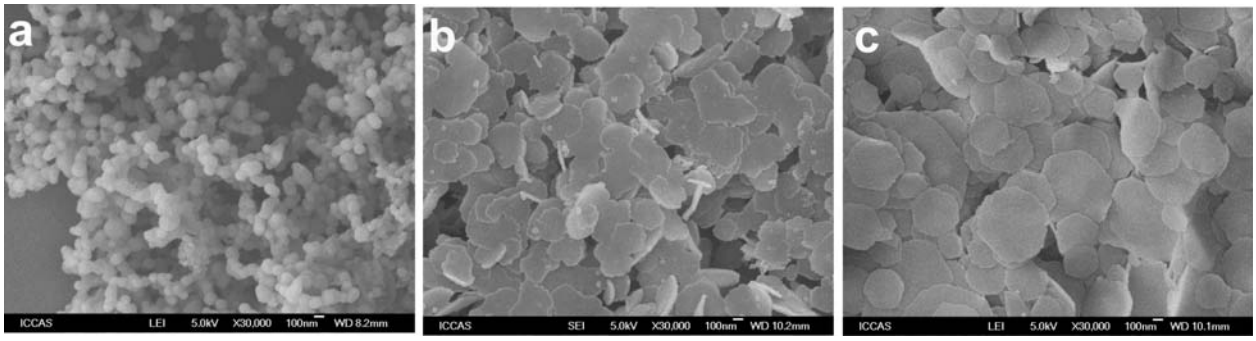

Fig. S7 Effects of PLL block on PEG-grafted silica morphology. SEM images of silica templated by (**a**) PEG_{45}-PLL_{15}, (**b**) PEG_{45}-PLL_{45}, (**c**) PEG_{45}-PLL_{100}. [Si]/[NH_3^+]=10, [phosphate]/[NH_3^+]=2.5.

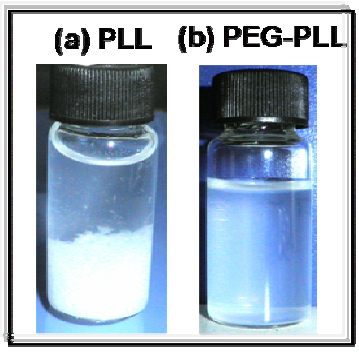

Fig. S8 Optical photos (a) Silica templated by PLL_{140} homopolypeptide and (b) silica templated by PEG_{45}-PLL_{100} diblock under identical conditions.

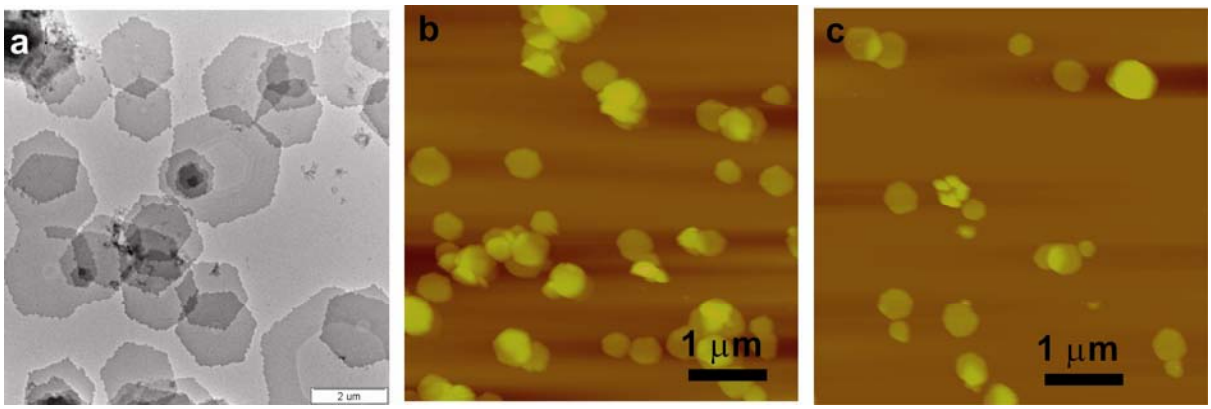

Fig. 9 (**a**) TEM image of silica nanoplates templated by PEG_{45}-PLL_{100} diblock; (**b**) and (b) AFM images of silica nanoplates templated by PEG_{45}-PLL_{140} diblock

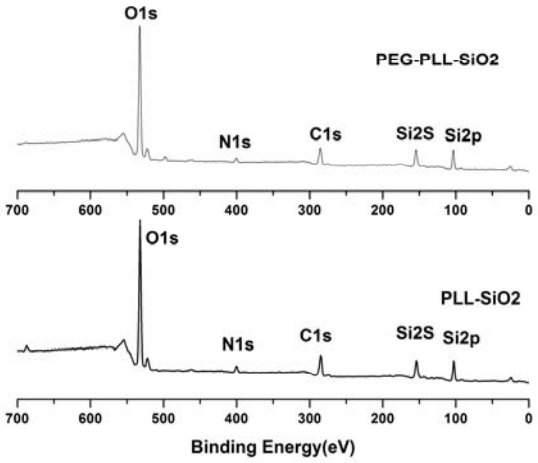

Fig. S10 XPS spectra of PEG_{45}-PLL_{100} directed silica nanoplates (top) and PLL homopolypeptide directed silica plates (bottom).

Table S2. XPS results of PEG_{45}-PLL_{100} and PLL_{140} directed silica nanoplates.

Element	PLL-SiO_2 (%)	PEG-PLL-SiO_2 (%)
C1s	23.23	21.75
O1s	51.89	54.04
N1s	3.84	2.65
Si2p	18.59	19.81

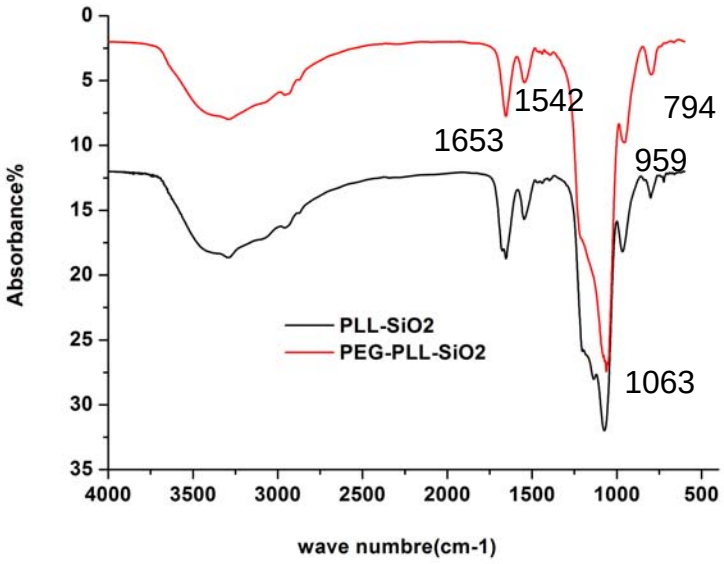

Fig. S11 FTIR spectra of PEG_{45}-PLL_{100} directed silica nanoplates (top) and PLL homopolypeptide directed silica plates (bottom).

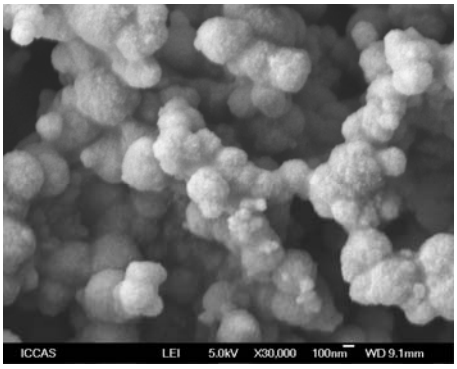

Fig. S12 SEM image of silica templated by $mPEG_{113}$-NH_2 homopolymer.

Furthermore, we analyzed the surface roughness of silica nanoplates directed by PEG_{45}-PLL_{140} diblock (Fig. 13) and PLL (DP=131) homopolypeptide (Fig. S14), respectively. The surface of silica nanoplates directed by PEG-PLL is relative smooth compared to those templated by PLL homopolypeptides. The reason we presume is that the former is coated with PEG chains while the latter is naked silica.

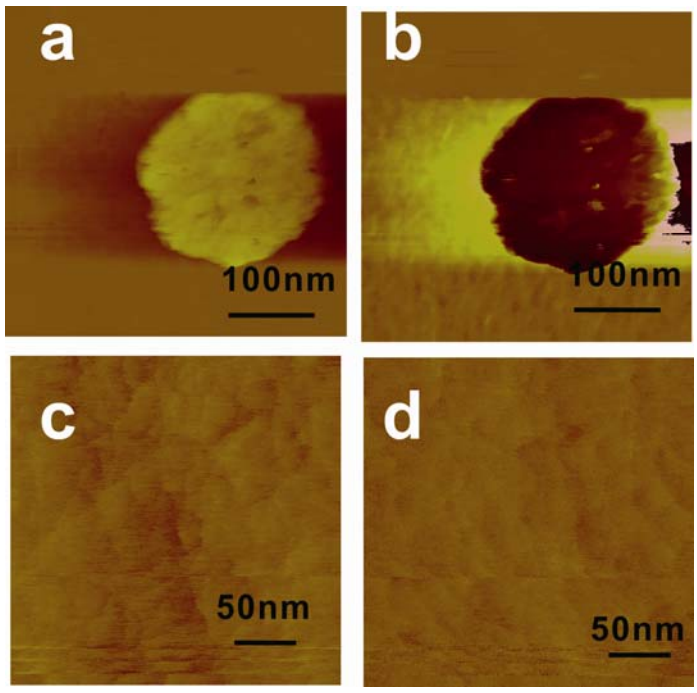

Fig. 13 AFM image of silica nanoplate templated by PEG_{45}-PLL_{140}. (**a, c**) height image, (**b, d**) phase image.

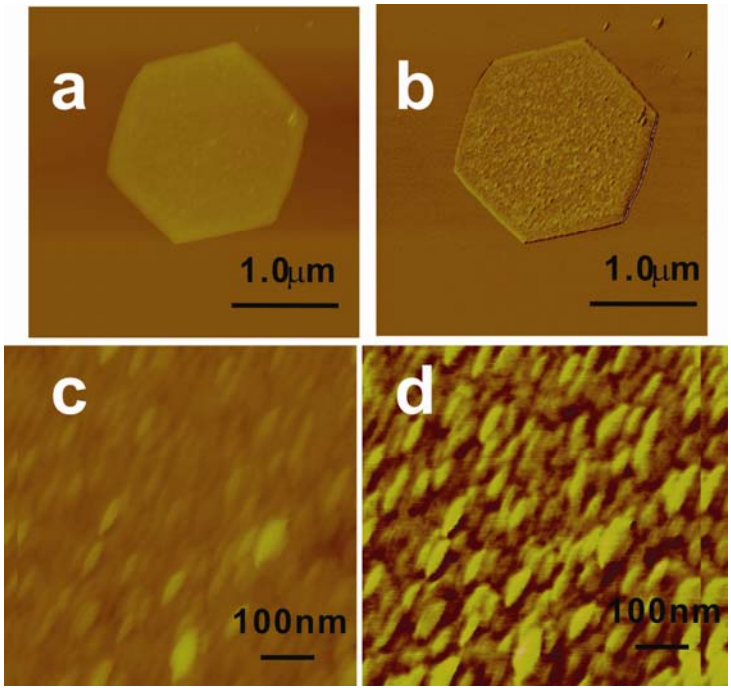

Fig. 14 AFM image of silica nanoplate templated by PLL_{131} homopolypeptide. (**a, c**) height image, (**b, d**) phase image.