Supporting Information for

Poly(N-cyanoethylethyleneimine): A New Nanoscale Template for Biomimetic Silicification

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Experimental Sections

Poly(2-ethyl-2-oxazoline) (MW=50,000) was purchased from Aldrich Co., Ltd. Hydrochloric acid (5.0 M), sulfonic acid (2.0 M), acetic acid, aqueous sodium hydroxide (1.0 M) and ammonia aqueous solution (28%) were purchased from Wako Pure Chemical Industry Ltd. Acrylonitrile and TMOS were purchased from TCI Co., Ltd. MS-51 (pentamer of TMOS) was purchased from Colcoat Co., Ltd. Iodobutylonitrile or iodovarelonitrile were synthesized from Finkelstein reaction of bromobutylonitrile or bromovarelonitrile with NaI in methylethylketone. These reagents and reactants were used without any purification. Commonly used solvents were obtained from commercial resources.

Preparation of linear poly(ethyleneimine-co-N-cyanoethylethyleneimine) P(EI-*co*-CEI) and PCEI

The linear poly(ethyleneimine) (LPEI) was synthesized by acidic hydrolysis of poly(2-ethyloxazoline) according to the literature procedure.[1] The P(EI-*co*-CEI) copolymers and PCEI were synthesized by cyanoethylation of secondary amines of LPEI with acrylonitrile (scheme 1). The LPEI dihydrate (0.8 g) dissolved in methanol (10 mL) was added a mixture solution of DMF (10 mL) and acrylonitrile (0.25, 0.5, 0.75, and 1.5 equivalents relative to ethyleneimine units in LPEI). The mixtures was degassed by bubbling with N_2 and then stirred at ambient temperature for 18h (0.25 and 0.5 equiv. of acrylonitrile) or at 60°C for 40 h (0.75 and 1.2 equiv. of acrylonitrile). The P(EI-*co*-CEI) copolymers and PCEI were obtained by precipitation from the resulting solution to ethylacetate, filtrated and dry up in vacuo at 60 ^{o}C for 5h.The yields were 79% (m=0.25, **1**), 94% (m=0.50, **2**),

77% (m=0.75, **3**), and 81% (m=n, **PCEI**).

PCEI : ^{1}H-NMR (CD$_3$CN, r.t., 300 MHz) δ 2.50 (t, J_{HH}=6.6, 2H), 2.55 (s, 4H), 2.78 (t, J_{HH}=6.6, 2H). ^{13}C-NMR (CD$_3$CN, r.t., 76 MHz) δ 17.1, 51.1, 53.3, 120.8 ppm. IR (KBr) ν 3422、3184、2955、2837、2243、1634、1463、1418、1373、1348、1258、1209、1118、1008、968、849、813、746 cm^{-1}. Mn=8300, Mw=23000, Mn/Mw=2.77. PCEI obtained showed bimodal from GPC profile which is similar to the bimodal peaks of precursor of poly(2-ethyl-2-oxazoline).

Preparation of poly(N-cyanopropylethyleneimine) (PCpEI) and poly(N-cyanobutylethyleneimine) (PCbEI)

The mixture solution of DMF/MeOH (1:1) was added LPEI dihydrate, 2.0 equiv. of triethylamine, and 1.5 equiv. of iodobutylonitrile (I-(CH$_2$)$_3$-CN) or iodovarelonitrile (I-(CH$_2$)$_4$-CN). The mixtures was degassed by bubbling with N$_2$ and then stirred at 55°C for 67 hrs. Protonated PCpEI and PCbEI were obtained by precipitation from the resulting solution to ethylacetate and dry up in vacuo at 80 ^{o}C.

Preparation of PCEI nanosheet and spherical aggregates.

Addition of distilled water (0.5 ml) to DMF (2 mL) solution containing PCEI (100 mg, 1.04 mmol) resulted in white precipitates. The mixture was heated to 60°C until the precipitate completely dissolved. The clear yellow solution was cooled down to room temperature and left for 1h. The solid fractions precipitated was washed with distilled water and collected by centrifugation. The purification was repeated three times to remove DMF. The wet white precipitates of PCEI nanosheet obtained was used for the silicification without drying. The precipitates after dried were conducted to the observations of TEM, SEM and AFM.

The spherical precipitates were performed in similar manner as described above

by addition of 0.8 mL of distilled water.

Silica deposition

The wet precipitates of PCEI (100 mg) were added to a mixture containing distilled water (20 mL) and silica source (MS-51 or TMOS, 1 mL). Then the mixture was stirred for 3 h at room temperature. The resulting silicas were washed with EtOH and collected by centrifugation (11,200×g, 10 min, 20 ^{o}C). This purification was repeated three times. The yields after dried up at 60°C in vacuo for 8h were 243 mg (from PCEI-NS), and 224 mg from PCEI-G, respectively.

The silica deposition using PCpEI and PCbEI as catalytic templates was tried on the similar procedure as described for silica deposition of PCEI aggregates. The resultanting precipitates formed sheet-like and sphere-like structures from PCpEI and sphere-like structure from PCbEI were observed by SEM (Figure S6).

Measurement

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 300 spectrometer. Chemical shifts were given in ppm relative to the internal solvent signal. Infrared spectra were recorded on a JASCO FT/IR-4200 spectrometer. Gel permeation chromatography (GPC) was performed on a Shodex GPC SYSTEM-11 using DMF as eluent relative to poly(methylmethacrylate) standards. The measurements of X-ray diffraction (XRD) were conducted on a Rigaku RX-7 diffractometer using Cu Kα radiation (λ=1.54Å). Differential scanning calorimetry was measured with a SII EXSTAR DSC7200 at a heating/cooling rate of 10°C/min in N_2 atmosphere. Scanning electron microscope (SEM) images were obtained using a Keyence VE9800 microscope. The sample was loaded on carbon-coated stubs and sputtered with Pt for imaging. High resolution transmission electron microscope (HR-TEM)

images were obtained with a JEOL JEM-2200 microscope. Atomic force microscope (AFM) images were obtained with a SII SPA400 and SPI4000 in dynamic force mode (DFM). The pH was measured with a digital pH-meter, which was calibrated at pH 4.01, 6.86, and 9.18 with standard buffers.
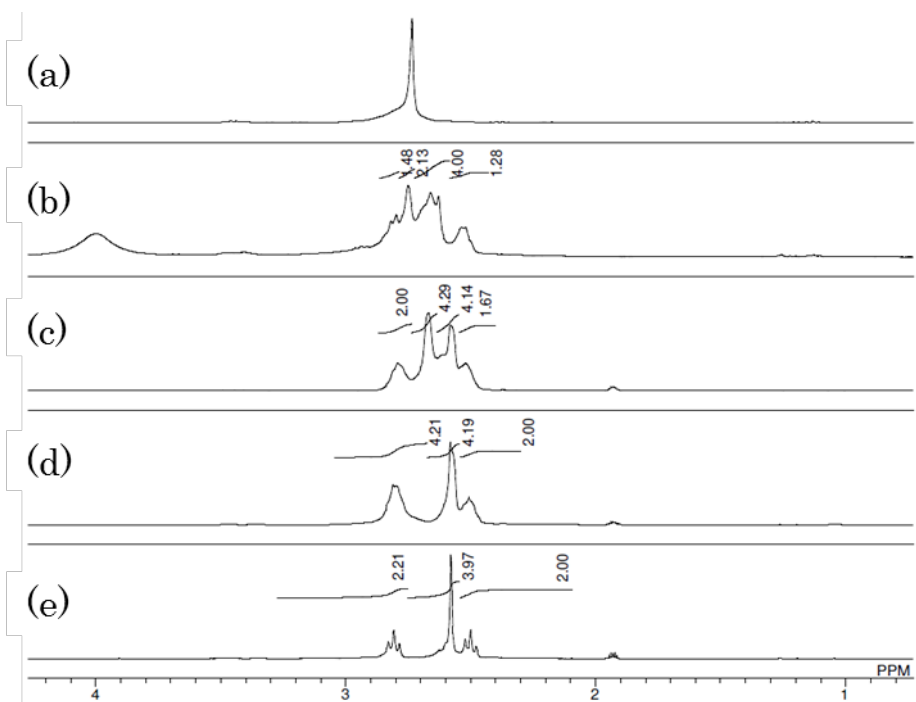
Fig. S1 ^{1}H-NMR spectra of (a) LPEI in CDCl$_3$ and the derivatives substituted by cyanoethyl group with (b) **1** in CDCl$_3$, (c) **2** and (d) **3** in CD$_3$CN, and (e) PCEI in CD$_3$CN.
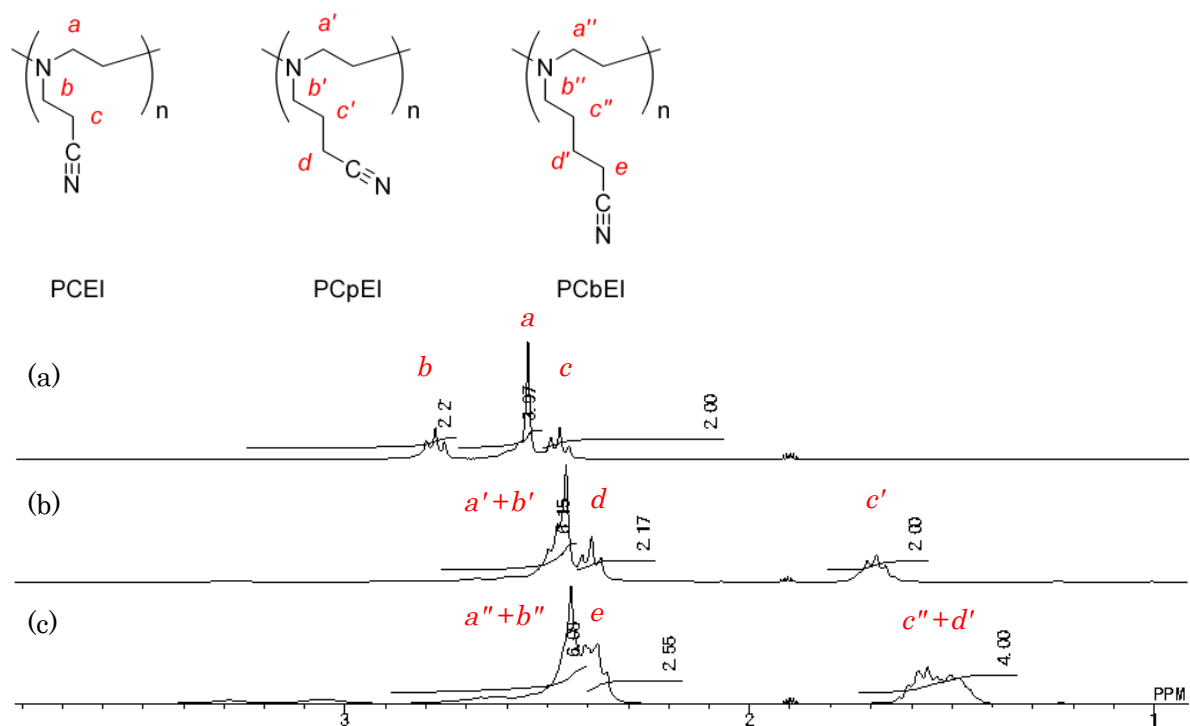
Fig S2. ¹H-NMR spectra of (a) PCEI, (b) PCpEI and (c) PCbEI in CD₃CN.
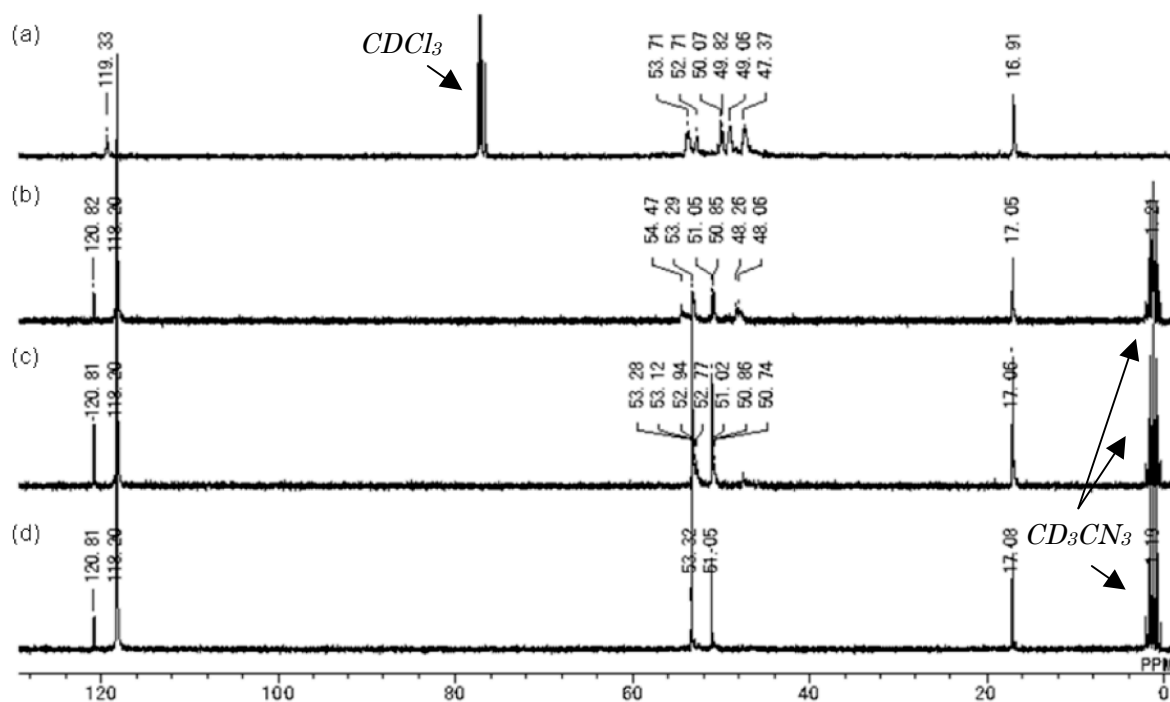
Fig. S3 ^{13}C-NMR spectra of the derivatives of LPEI substituted by cyanoethyl group with (a) **1** in CDCl$_3$, (b) **2**, and (c) **3** in CD$_3$CN, and (d) PCEI in CD$_3$CN.

^{13}C-NMR spectra of all derivatives show two peaks due to the carbon of cyano group and methylene next to cyano group around 120 ppm and 17 ppm, respectively. In ^{13}C-NMR spectrum of PCEI, each methylene signal bonded to N on ethyleneimine unit -CH$_2$CH$_2$-N- CH$_2$CH$_2$CN was observed at 51.1 ppm and 53.3 ppm, respectively. The polymers of **1** and **2** with different substitution ratio of cyanoethyl group have two monomeric units, the signals due to methylene carbon on ethyleneimine units appeared around 47~54 ppm with multiple.
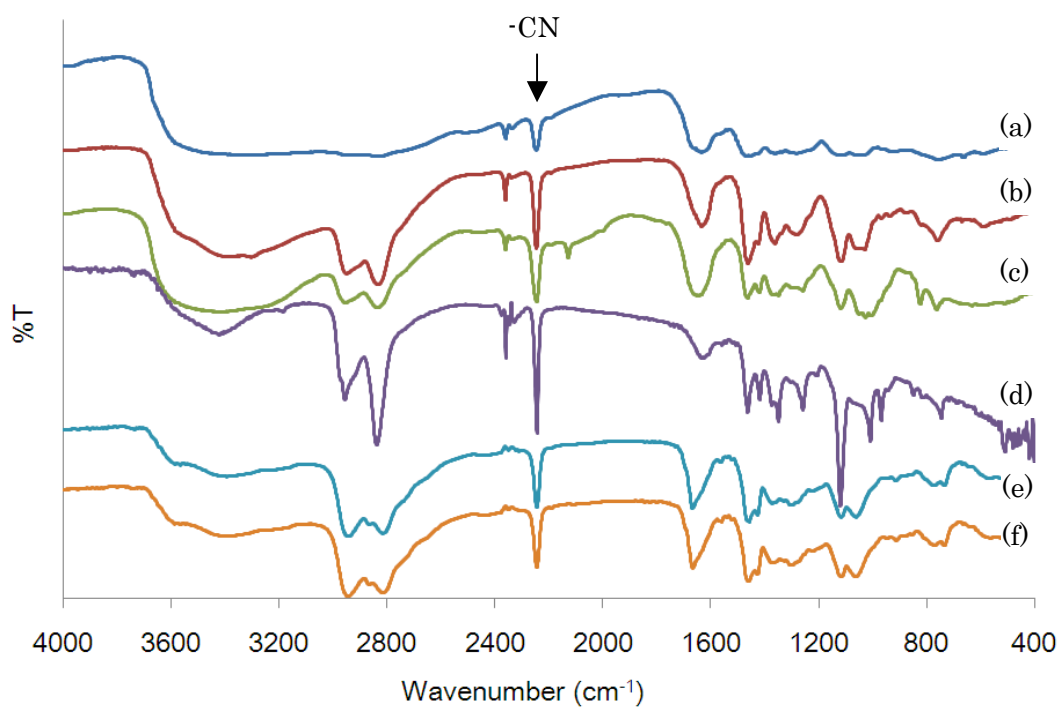
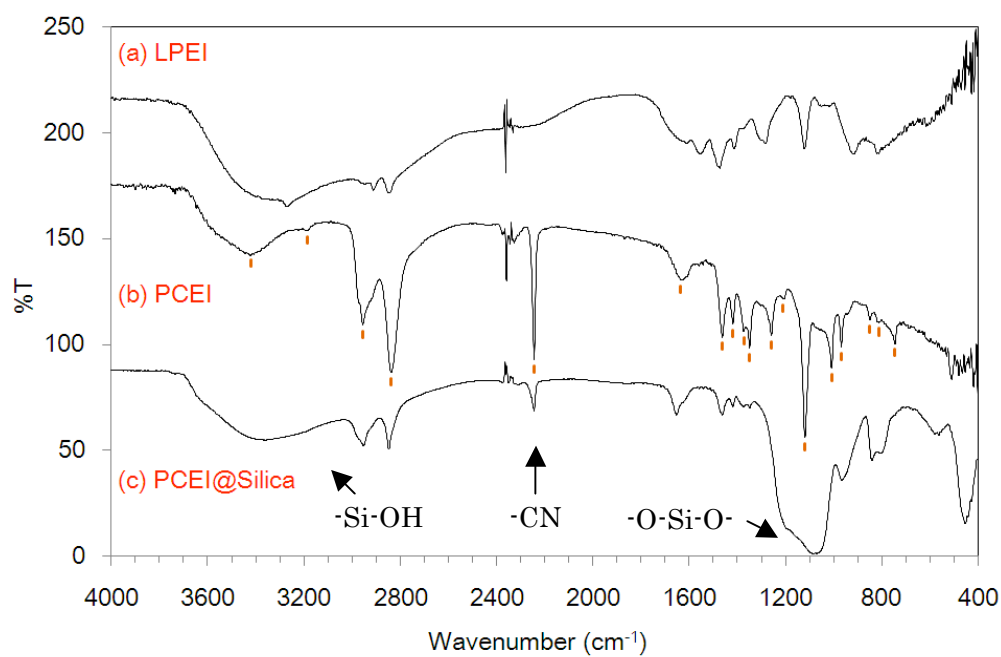Fig. S4 FT-IR spectra of (a) **1**, (b) **2**, (c) **3** , (d) PCEI, (e) PCpEI, and (f) PCbEI.

Fig. S5 FT-IR spectra of (a) LPEI dihydrate, (b) PCEI, and (c) Silica prepared from PCEI nanosheet.
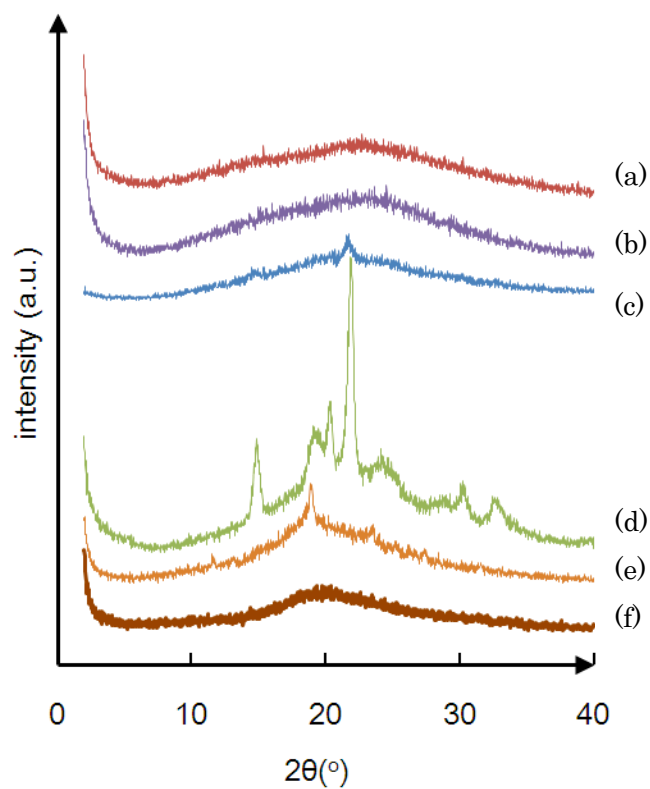
Fig. S6 XRD patterns of (a) **1**, (b) **2**, (c) **3**, (d) PCEI, (e) PCpEI, and (f) PCbEI. The diffractions of (d) PCEI were appeared at 2θ=14.8, 19.1, 20.3 and 21.9°.
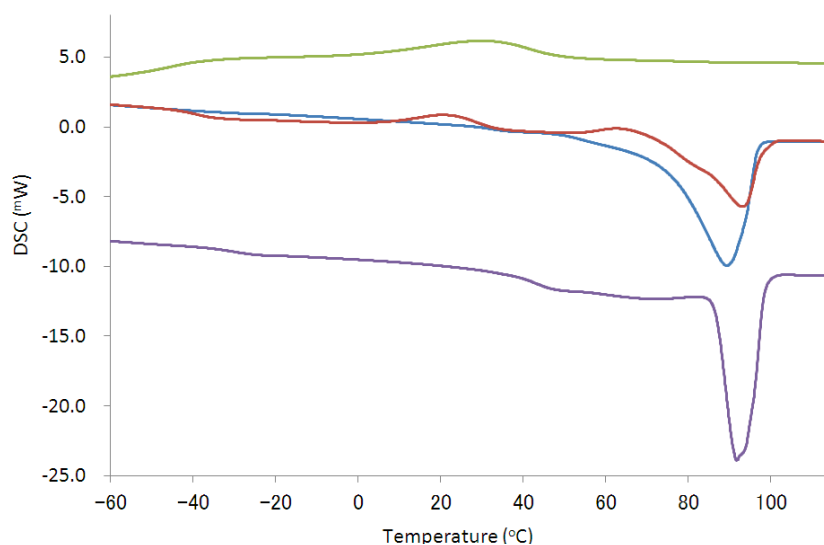
Fig. S7. DSC curves of PCEI precipitate (purple line) and PCEI nanosheet prepared by recrystallization in DMF/H$_2$O (blue, green, and red lines). The blue, green and red lines are from the first heating run, the cooling run and the second heating run, respectively.

DSC analysis revealed two endothermic points in the temperature range of 25~80°C with the small peaks at 49.0°C and 68.4°C, and an strong endothermic peak at melting point of 91.7°C for the PCEI precipitate. The endotherm at lower temperature would be due to the presence of PCEI crystallites with low crystalline degree. DSC trace of the PCEI nanosheet shows an endothermic broad line with the maximum point at 89.5°C from the first heating run. After cooling, the maximum point was shifted to 92.8°C and endothermic lines of Tg was observed around -20°C and 40°C from the second heating run.

Solubility of the PCEI in different solvents

Table S1. Solubility of PCEI.

Solvent	Ratio (mL)	r.t.	heating (°C)
Water	20	-	- (90)
DMF	20	+	+
Methanol	20	-	- (60)
DMF/Water	5 / 15	-	+ (90)
DMF/Methanol	15 / 5	-	+ (60)
DMF/Methanol	10 / 10	-	+ (60)

PCEI / Solvent ,0.192 mg / 20 mL
+ : soluble, - : insoluble
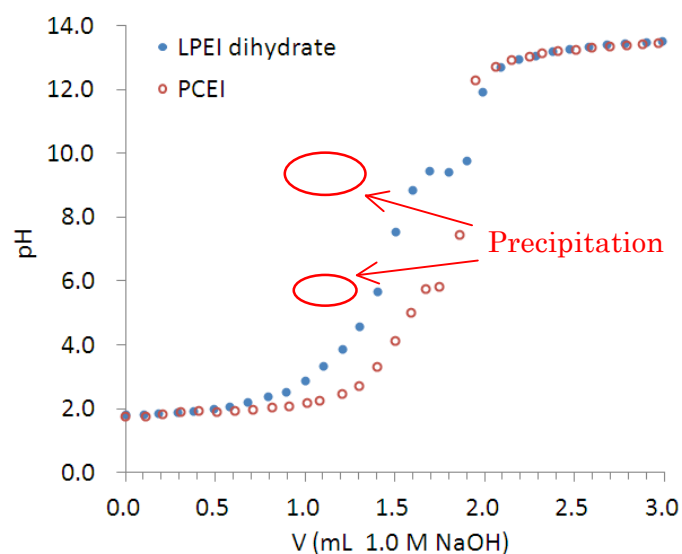
Fig. S8. Titration curves for LPEI dihydrate and PCEI (c = 0.1 mol/L) at 20 °C. Acid solution of 0.50 M HCl (aq) and basic solution of 1.0 M NaOH (aq) was used for the titration. Since both LPEI and PCEI contain basic amino groups in the polymer chain, they are soluble in water under acidic conditions (pH < 5). Titration of an acidic solution of LPEI with 1.0 M NaOH (aq) gave crystalline LPEI with poor solubility in water at pH = 9~10. The titration experiment for PCEI is different to that of LPEI, forming insoluble crystalline PCEI under weak acidic conditions (pH = 5~6).

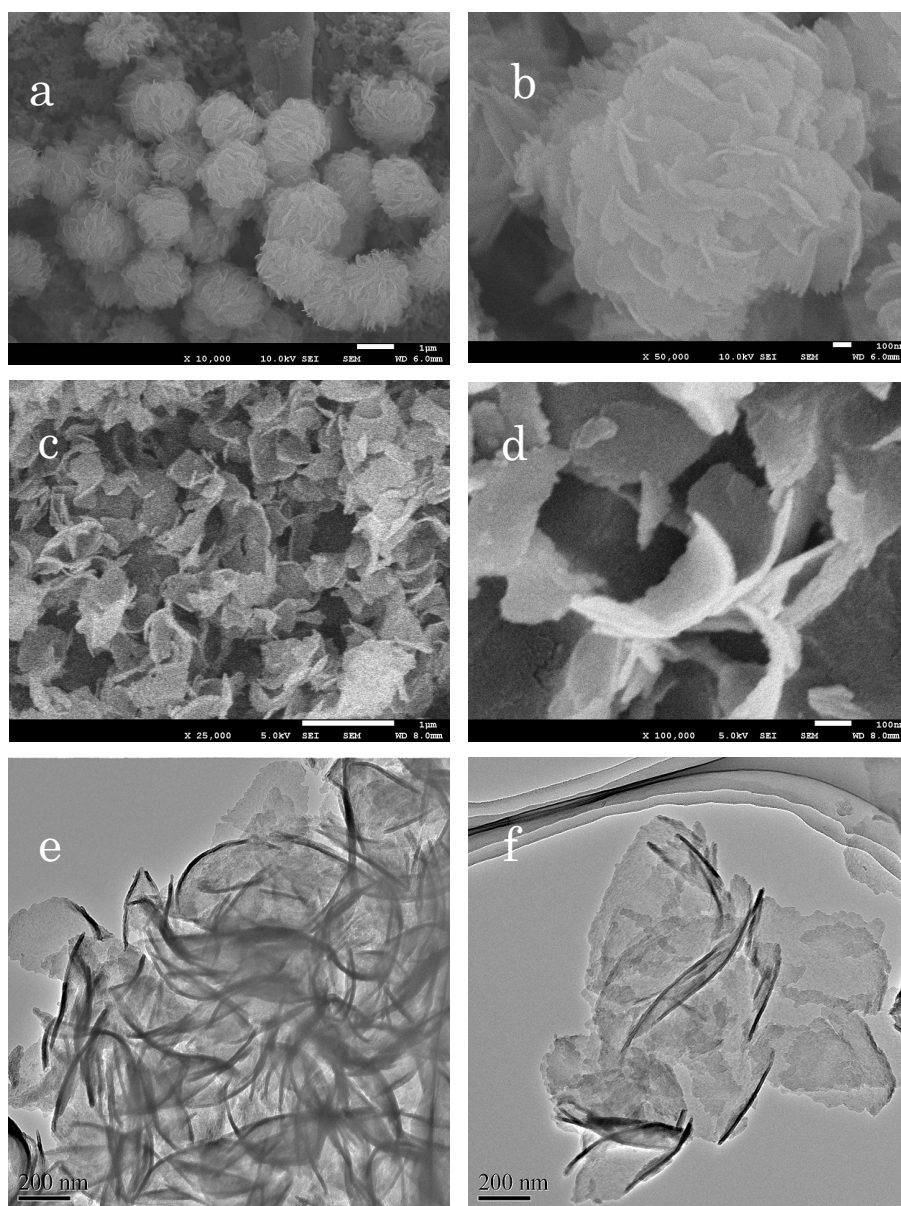Fig. S9. SEM images of globular silica (a, b) obtained from calcination of SiO$_2$@PCEI-G at 800°C for 3 h. SEM (c, d) and TEM (e, f) images of nanosheet silica obtained from calcination of SiO$_2$@PCEI-NS at 800°C for 3 h.
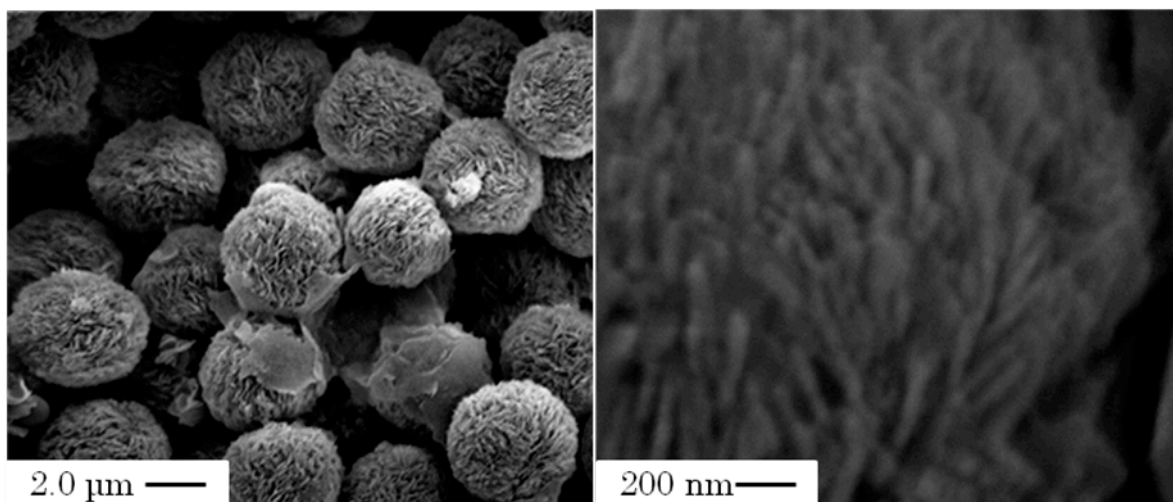
Fig. S10. SEM images of silica prepared from **3** (left) and high magnification (right). The yields of silica were 95%.
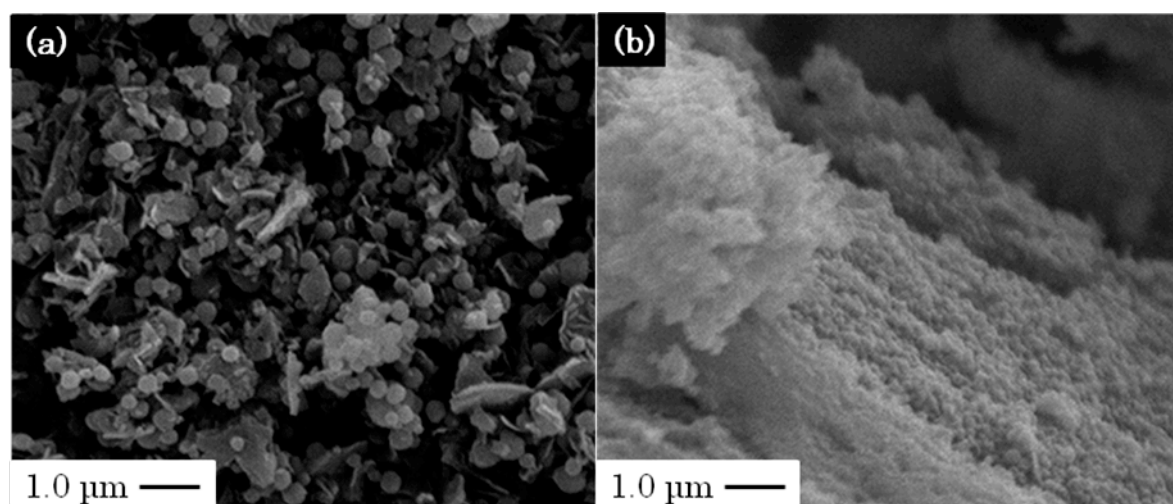

Fig. S11. SEM images of precipitates after silica deposition from (a) PCpEI and (b) PCbEI. The yields of silica were 85% and 41%, respectively, for PCpEI and PCbEI systems.

References

1. a) J.-J. Yuan, and R.-H. Jin, *Langmuir,* 2005, **21**, 3136. b) R.-H. Jin, and J.-J. Yuan, *Polymer J.*, 2007, **39**, 464. c) J.-J. Yuan, P.-X. Zhu, N. Fukazawa, and R.-H. Jin, *Adv. Funct. Mater.*, 2006, **16**, 2205.