Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Biomimetic silica deposition promoted by sub-5 μm complexes of dicarboxylic acids/polyethyleneimine microballs: a new approach of tuning silica structures using messenger-like organic acids

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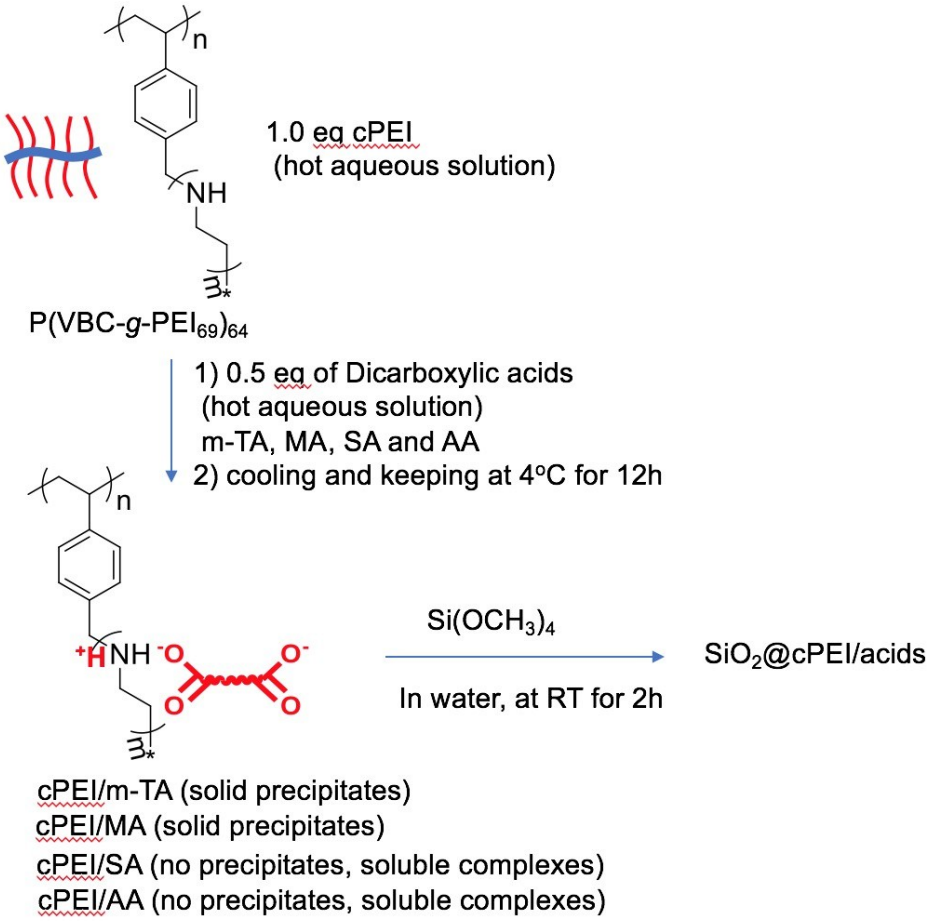
Control experiments of complexations and silica deposition employing comb-like polyethylemneimine cPEI.

1) General scheme of control experiments



2) Complexation of cPEI with meso-tartaric acid

Comb-like polymer P(CMS-*g*-$PEI_{69})_{64}$ (cPEI) was prepared according to our previous reports (D.-D. Yao and R.-H. Jin, *Polym. Chem*., 2015, **6**, 2255-2263; D.-D. Yao, H. Kubosawa, D. Soma and R.-H. Jin, *Polymer*, 2016, **86**, 120-128). The preparation of cPEI/m-TA complex was as follows: Firstly, the mixture containing cPEI (0.04 g, 0.5 mmol) and water (5 mL) was heated up to about 80 °C to dissolve cPEI. To this cPEI hot solution, a hot aqueous solution containing m-TA (0.25 mmol, 0.04 g) and water (5 mL) was added, and stirred at 80 °C for 5 min. After then, naturally cooled, and allowed to stand at room temperature, and adjusted to pH 4 with NH_3 or HCl. Then, this mixture was cooled and left at 4 °C for 12 h. Finally, the precipitates were corrected by centrifugation, and washed with distilled water and acetone, and dried under ambient condition.

3) Complexation of cPEI with mucic acid

A mixture containing cPEI (0.04 g, 0.5 mmol) and 1M HCl (10 mL) were heated up to about 80 ^{o}C to obtain cPEI solution. To this solution, a hot solution of DA (0.25 mmol) dissolved in 1M NH_3 (10 mL) was added, and stirred at 80 ^{o}C for 5 min. After naturally cooling to room temperature, the pH value of the mixture was adjusted about 3 with NH_3 or HCl. Then, this mixture was cooled and left at 4 ^{o}C for 12 h. The precipitates were collected by centrifugation, and washed with distilled water and acetone, and finally dried under ambient condition.

4) Silica hybridization of cPEI/m-TA (MA) with TMOS

TMOS (1 mL) was added into a dispersion of cPEI/*m*-TA (or MA) in water (10 mL) followed by stirred at room temperature for 2 h. After then, the precipitates were collected by centrifugation, and washed with distilled water and acetone, finally dried under room temperature.

5) Silica deposition in complexes solution of cPEI/SA (or AA)

A mixture containing cPEI (0.04 g, 0.5 mmol) and water (10 mL) was heated up to about 80 ^{o}C to dissolve cPEI. To this cPEI hot solution, a hot aqueous solution of succinic acid (or adipic acid) (0.25 mmol) dissolved in water (10 mL) was added, and stirred at 80 ^{o}C for 5 min. After that, naturally cooled, and allowed to stand at room temperature. And then TMOS (1 mL) was added into the complex solution, stirred at room temperature for 2 h. Taking 1 mL of liquid from the resulting opaque solution into 3 mL of ethanol and the mixture was cast on silicon wafer and dried at room temperature for SEM observation.

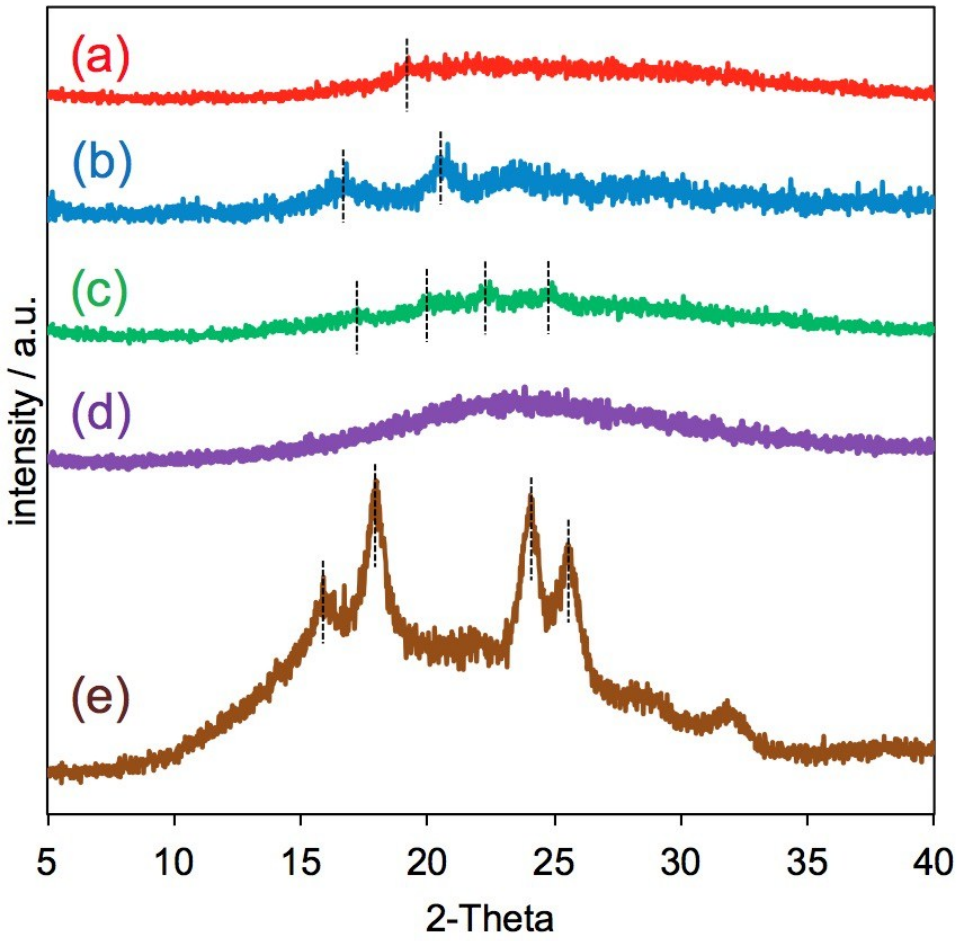


Fig. S1. XRD patterns of μ-PSt-*g*-LPEI (e) and μ-PSt-*g*-PEI/dicarboxylic acids complexes associated with m-TA (a), MA (b), SA (c) and AA (d).

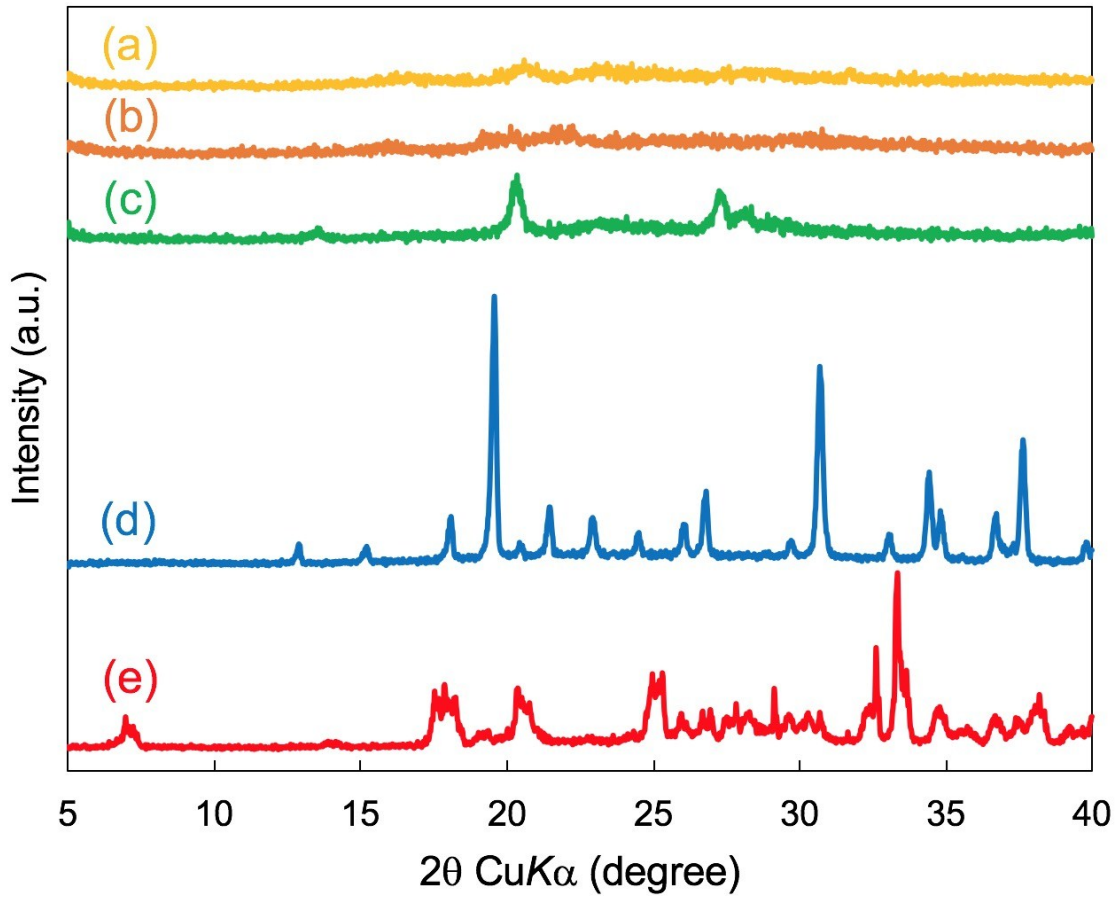


Fig. S2. XRD patterns of (a) cPEI/*m*-TA (b) cPEI/MA, (c) cPEI, (d) MA, (e) *m*-TA.

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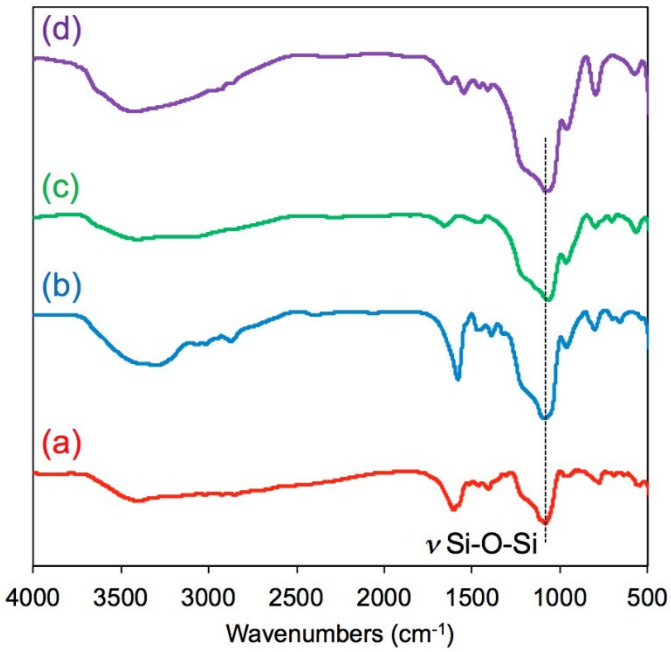

Fig. S3. FT-IR spectra of (a) m-PSt-g-PEI/m-TA@SiO_2 (b) m-PSt-g-PEI/MA@SiO_2 (c) m-PSt-g-PEI/SA@SiO_2 and (d) m-PSt-g-PEI/AA@SiO_2 .

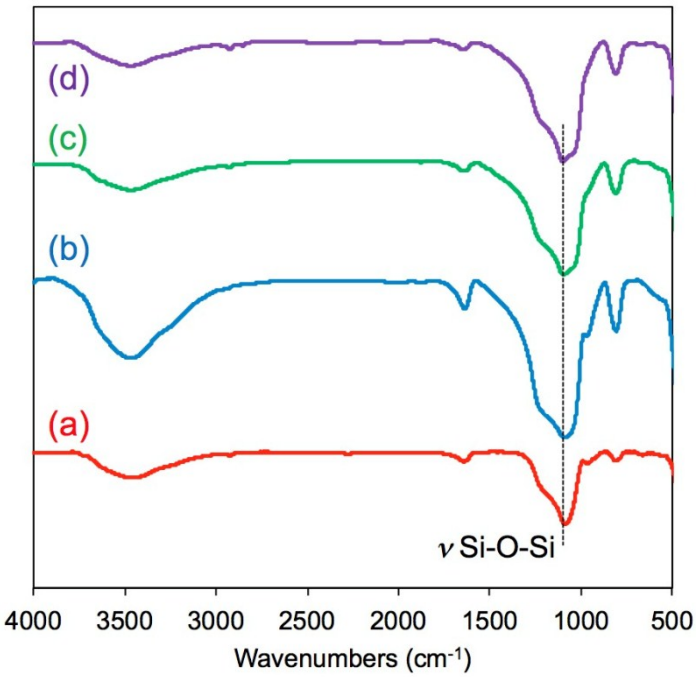

Fig. S4. FT-IR spectra after calcination of *m*-PSt-*g*-PEI/dicarboxylic acid@SiO_2. (a) m-TA, (b) MA, (c) SA, (d) AA.

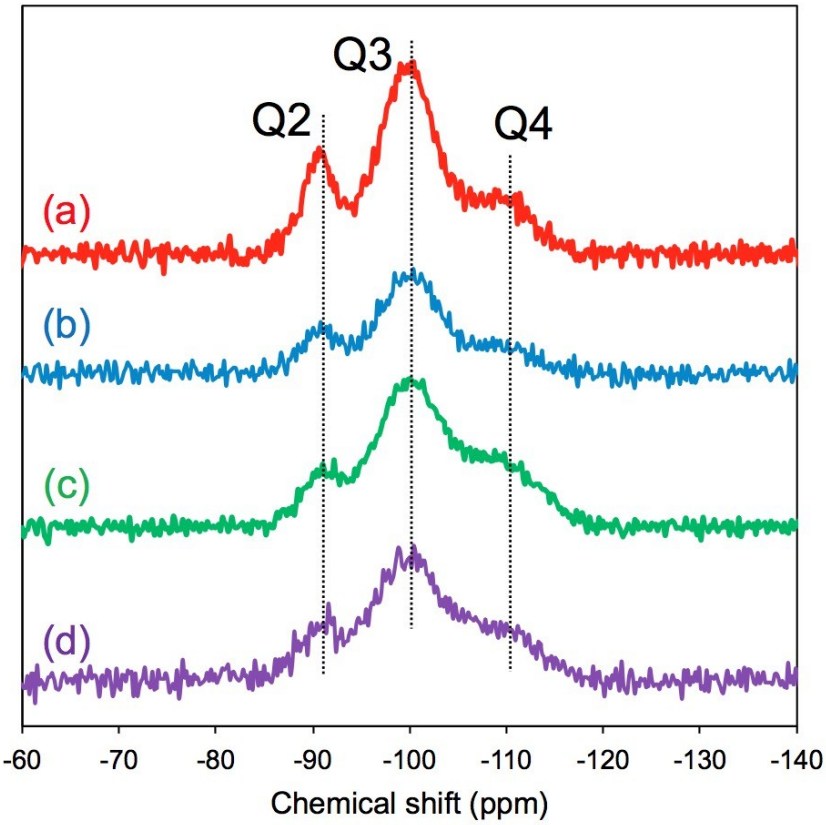

Fig. S5. ^{29}Si CP/MAS NMR spectra of calcined μ-PSt-*g*-PEI/dicarboxylic acid@SiO_2. (a) m-TA, (b) MA, (c) SA, (d) AA..

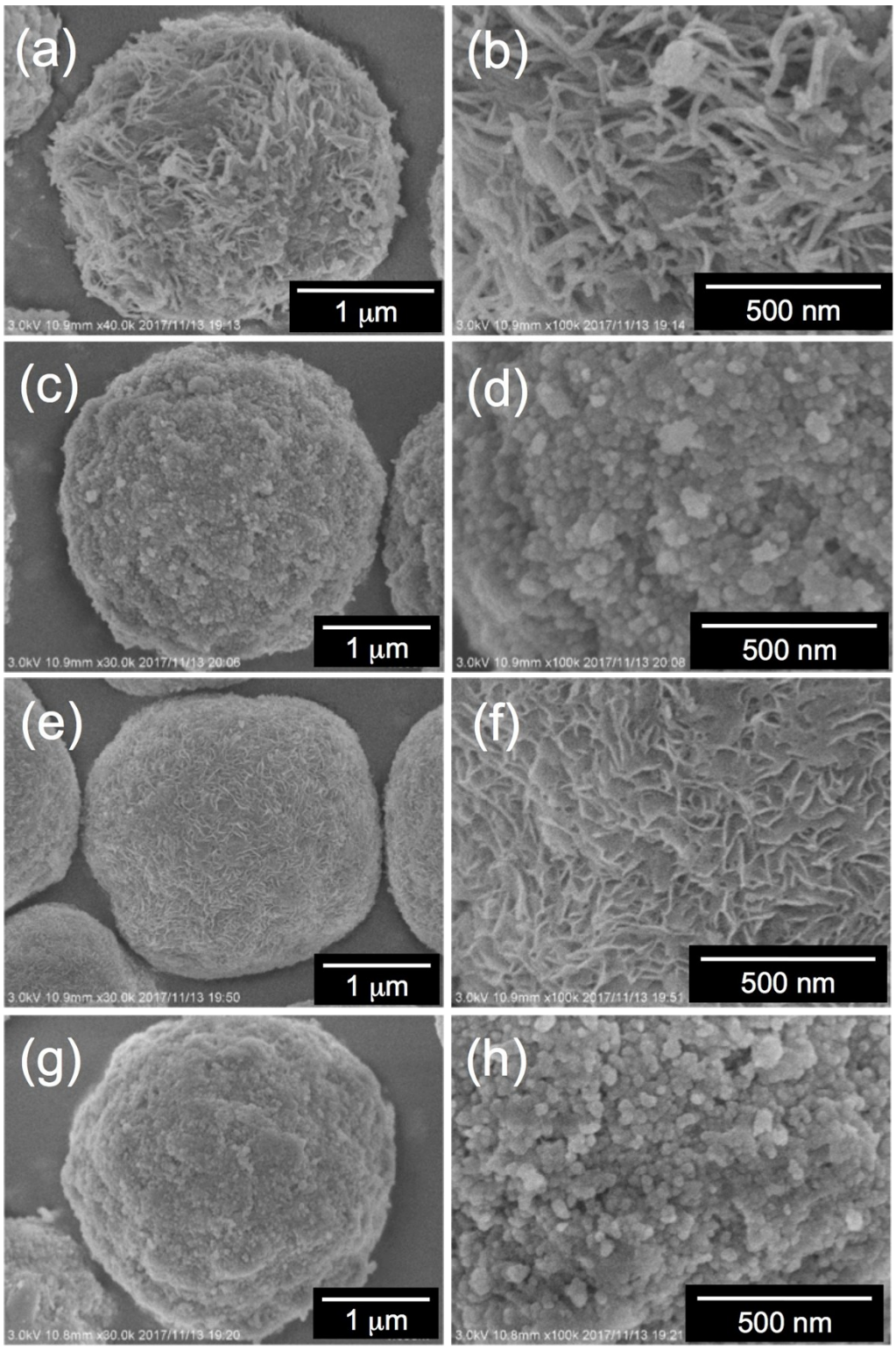

Fig. S6. SEM images (of magnified areas) after calcined of μ-PSt-*g*-PEI/DD@SiO_2. DD (dicarboxylic acid): (a, b) m-TA, (c, d) SA, (e, f) MA, (g, h) AA.

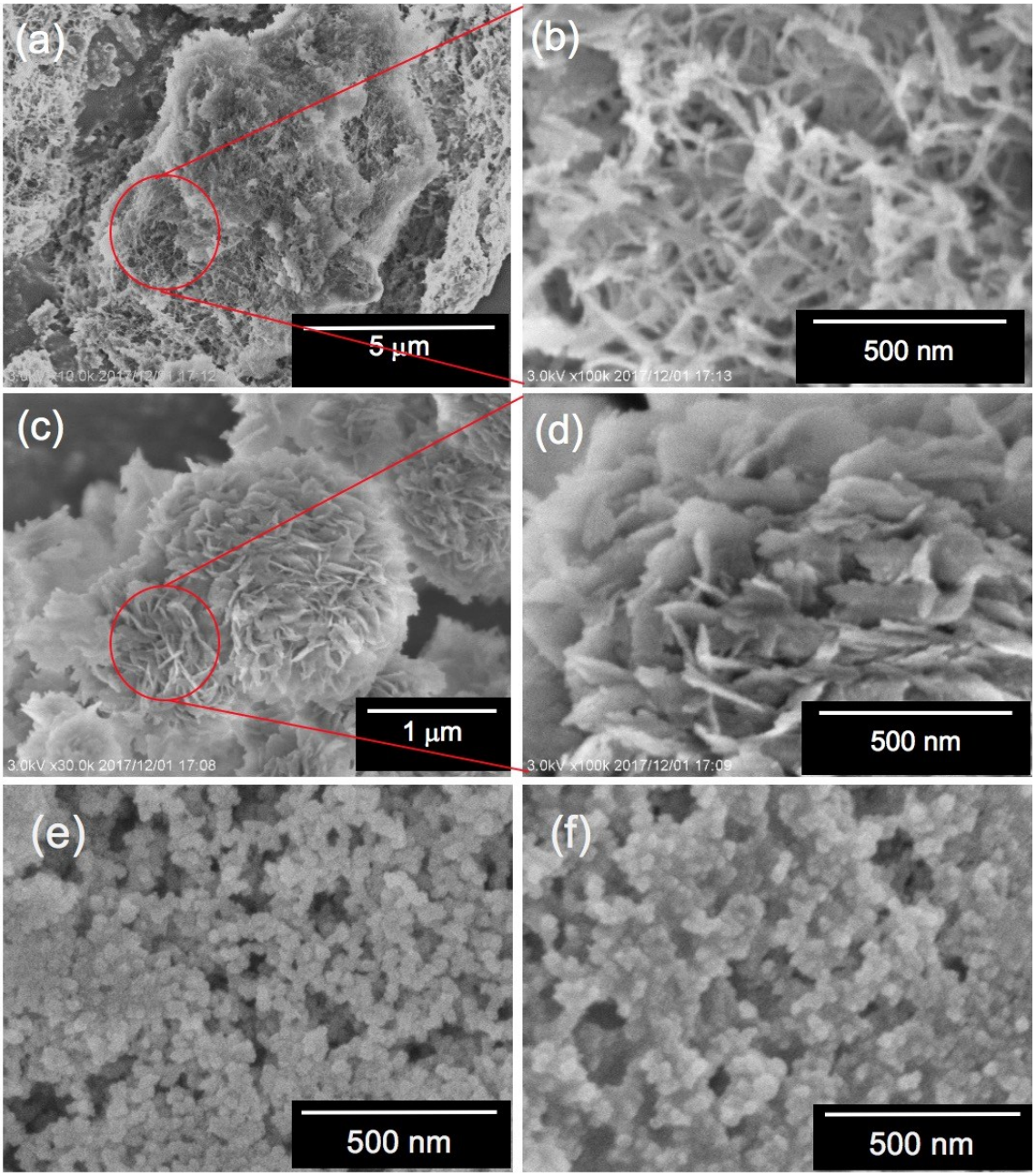

Fig. S7. SEM images of the silica powders templated by the complexes of cPEI/*m*-TA (a, b), cPEI/MA (c, d), cPEI/SA (e) and cPEI/AA (f). The images of (b) and (d) are the magnified observation from the red-circular areas, respectively.

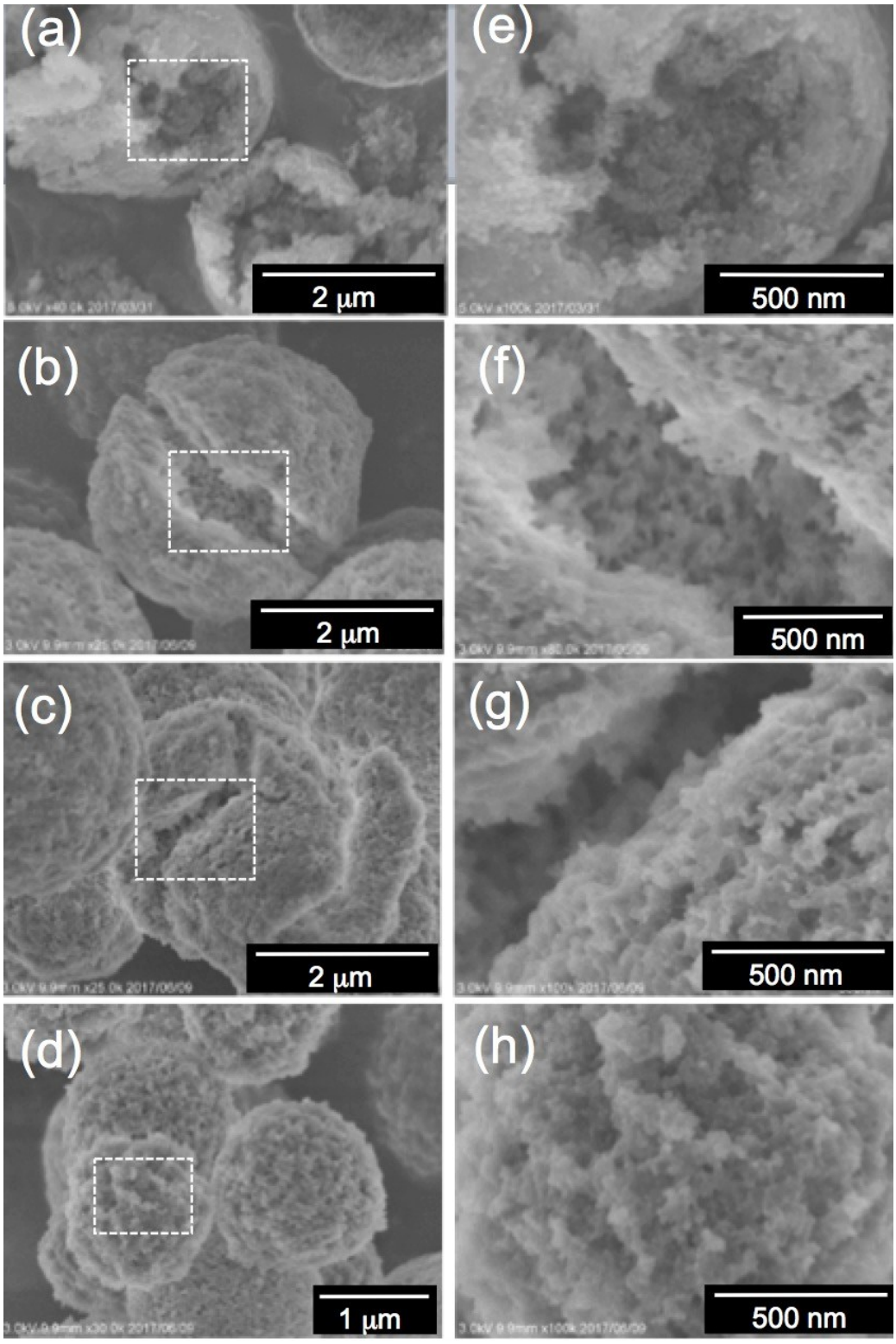

Fig. S8. SEM images (of magnified area) after APS treatment of calcination of μ-PSt-*g*-PEI/dicarboxylic acid@SiO_2 mediated by different kinds of dicarboxylic acid: (a, e) m-TA, (b, f) SA, (c, g) MA, (d, h) AA.

Table S1. BET surface area of the calcined μ-PSt-*g*-PEI/dicarboxylic acid@SiO_2

Organic acid	BET surface area (m^2/g)
Mesotartaric acid	430.0
Succinic acid	133.3
Mucic acid	615.0
Adipic acid	96.7

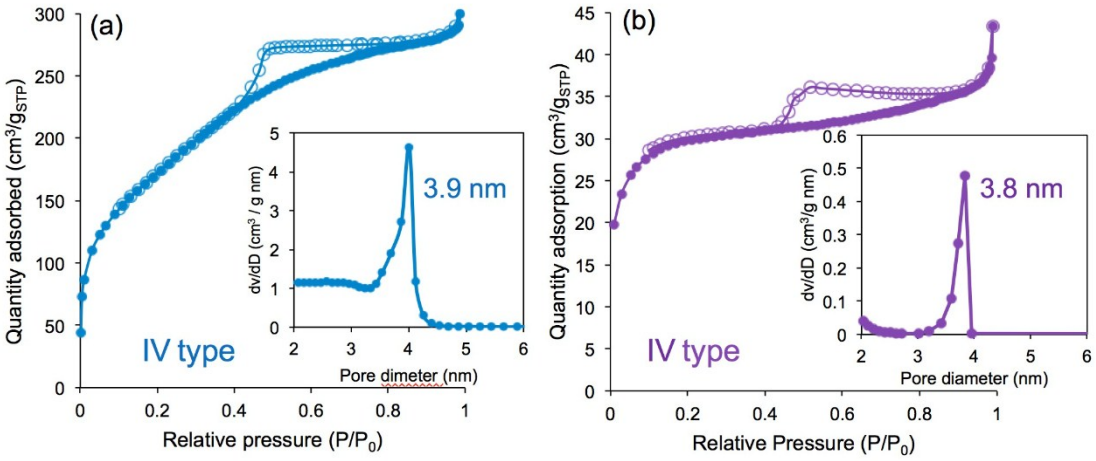

Fig. S9. N_2 adsorption desorption isotherms and pore size distribution of the calcined of μ-PSt-*g*-PEI/dicarboxylic acid@SiO_2 mediated from (a) Mucic acid, (b) Adipic acid. Open dots: desorption; close dots: adsorption.