Electronic Supplementary Information

Millipede-inspired Structural Design Principles for High Performance Polysaccharide Binders in Silicon Anodes

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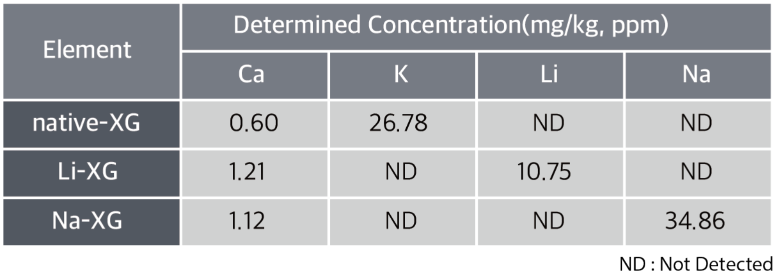
Materials and Chemicals. Si nanopowder with average particle size of 60 nm was donated from KCC (Korea). Graphite powder (particle size ~2 μm) for the preparation of Si/Graphite composite was donated from Kokam (Korea). SuperP was purchased from Timcal (Switzerland). Xanthan gum was purchased from Tokyo Chemical Industry Co. (Japan). Cellulose, amylose, amylopectin, Na-CMC, and alginate were purchased from Sigma-Aldrich (USA). $LiOH·H_2O$ and NaOH were purchased from Samchun (Korea). Dialysis tubing was purchased from Cellu-Sep with a molecular weight cut-off of 5 kDa. Fourier transform infrared (FTIR) spectra were recorded on Shimadzu FT-IR spectrometer (IRTracer-100).

Li/Na-xanthan gum. Li/Na-XG was obtained upon hydrolysis of native-XG. For Li-XG, 0.3 g of $LiOH·H_2O$ was added to 100 mL aqueous solution of native-XG (0.4 g). The solution was stirred at room temperature for 24 h. The polymer was purified by dialysis (MWCO, 5 kDa) for 24 h and subsequently lyophilized. For Na-XG, the same procedure was repeated with NaOH (0.3 g) instead of $LiOH·H_2O$.

Chemical/structural/mechanical/thermal characterization. For preparation of the specimen for SPM imaging (XE-100, Park Systems, Korea), each polymer was completely dispersed in deionized water with concentration of 1 μg/mL and the dispersion was dropped onto 1x1 cm^2 boron-doped p-type Si wafer and was dried at room temperature. The images were obtained under non-contact mode. For electrode peeling tests, the 3M tape was attached to each of 1 x 3 cm^2 Si electrodes shown in Figs. 3a-c. The peeling strengths during detachment of the 3M tape were recorded on a high-precision micromechanical test instrument (Delaminator Adhesion Test System; DTS Company, Menlo Park, CA, USA), generating load-displacement plots. The thermal property of native-XG was characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), recorded by a DTA-60A apparatus (Shimadzu Corporation, Japan). The temperature was scanned from 30 °C to 300 °C at a rate of 10 °C min^{-1} under a nitrogen flow at 50 mL min^{-1}.

Electrochemical tests. For the Si electrode preparation, slurries were prepared at a ratio of Si : binder : SuperP = 60 : 20 : 20 wt% in deionized water for polysaccharide binders including cellulose, amylose, amylopectin, native-XG, renatured-XG, Na-CMC, alginate, Li-XG, and Na-XG. All of the slurries have good dispersion. Each slurry was cast on copper foil and was then dried in a vacuum oven at 30 °C overnight. The mass loading of Si was 0.3 mg cm^{-2} or 0.9 mg cm^{-2}. 2032 coin cells were used for galvanostatic measurements. Li metal was used as both counter and reference electrodes, and 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC) : diethylene carbonate (DEC) in 50 : 50 v% with 5 wt% fluoroethylene chloride (FEC) was used as an electrolyte (PANAX ETEC, Korea). Polyethylene film (SK, Korea) was used as separator, and all the cells were aged for at least 3 h before cycling tests. The battery assembly was conducted inside an argon-filled glove box. For Si/graphite blend electrode preparation, Si and graphite were first ball-milled (200 rpm) at a ratio of 20 : 80 wt% at room temperature overnight. For slurry preparation, Si/graphite blend : binder : SuperP were mixed at 80 : 10 : 10 wt% in deionized water, and the slurries were cast onto Cu foil. Si/graphite mass loading was 1.0 mg cm^{-2}. For SEM imaging of electrode surface, all electrodes after battery cycling were thoroughly rinsed with EC: DEC mixture (50 : 50 v%) to eliminate remaining Li salts on the electrode surfaces and then dried for 6 h inside an Ar-glove box. Field-emission SEM (Hitachi, Japan) was used for visualization of the surface morphology and all of the SEM images in Fig.4 were taken at 45 degree tilted angle. For higher magnification SEM images in Fig. 5 and Fig. S10, the same electrode samples in Fig. 4 were used and the electrodes were coated with Pt (thickness: ~5 nm) to increase the electronic conductivity.



Element	Determined Concentration(mg/kg, ppm)			
	Ca	K	Li	Na
native-XG	0.60	26.78	ND	ND
Li-XG	1.21	ND	10.75	ND
Na-XG	1.12	ND	ND	34.86

ND : Not Detected

Table. S1 Cation concentrations determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

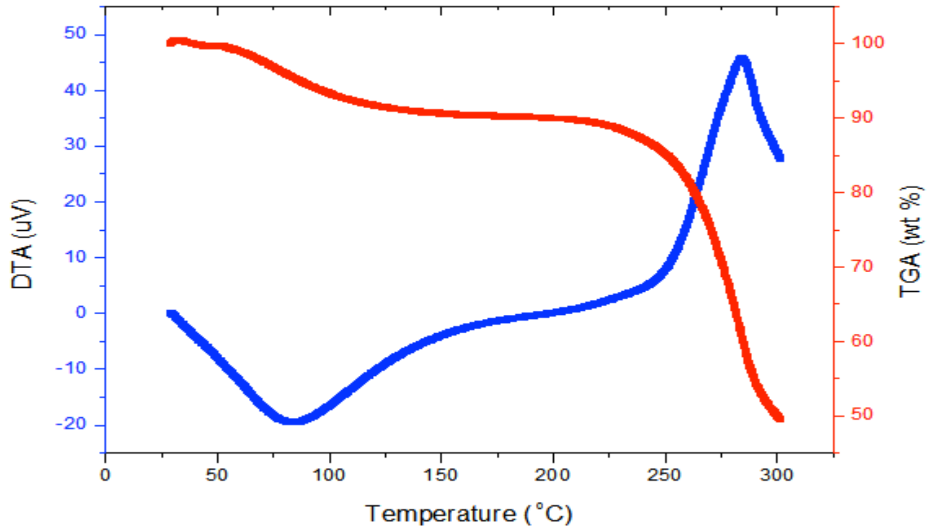


Fig. S1 TGA and DTA profiles of native-XG.

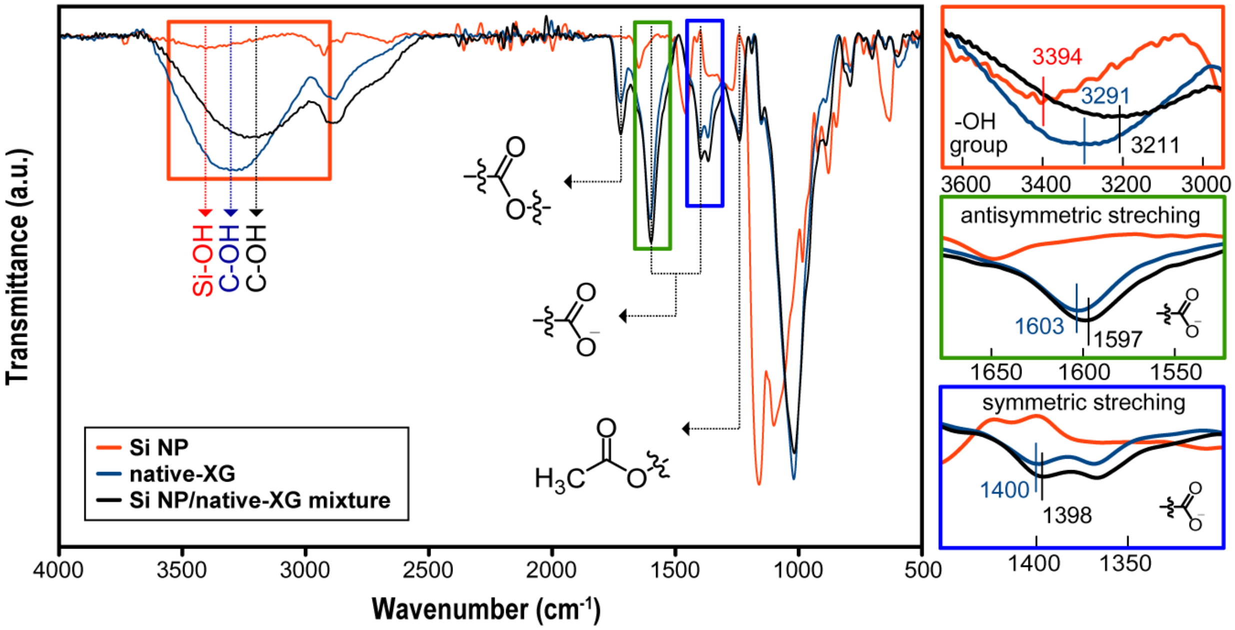


Fig. S2 FTIR spectra of Si NP, native-XG, and Si NP/native-XG mixture to verify ion-dipole and hydrogen bonding interactions between Si and native-XG.

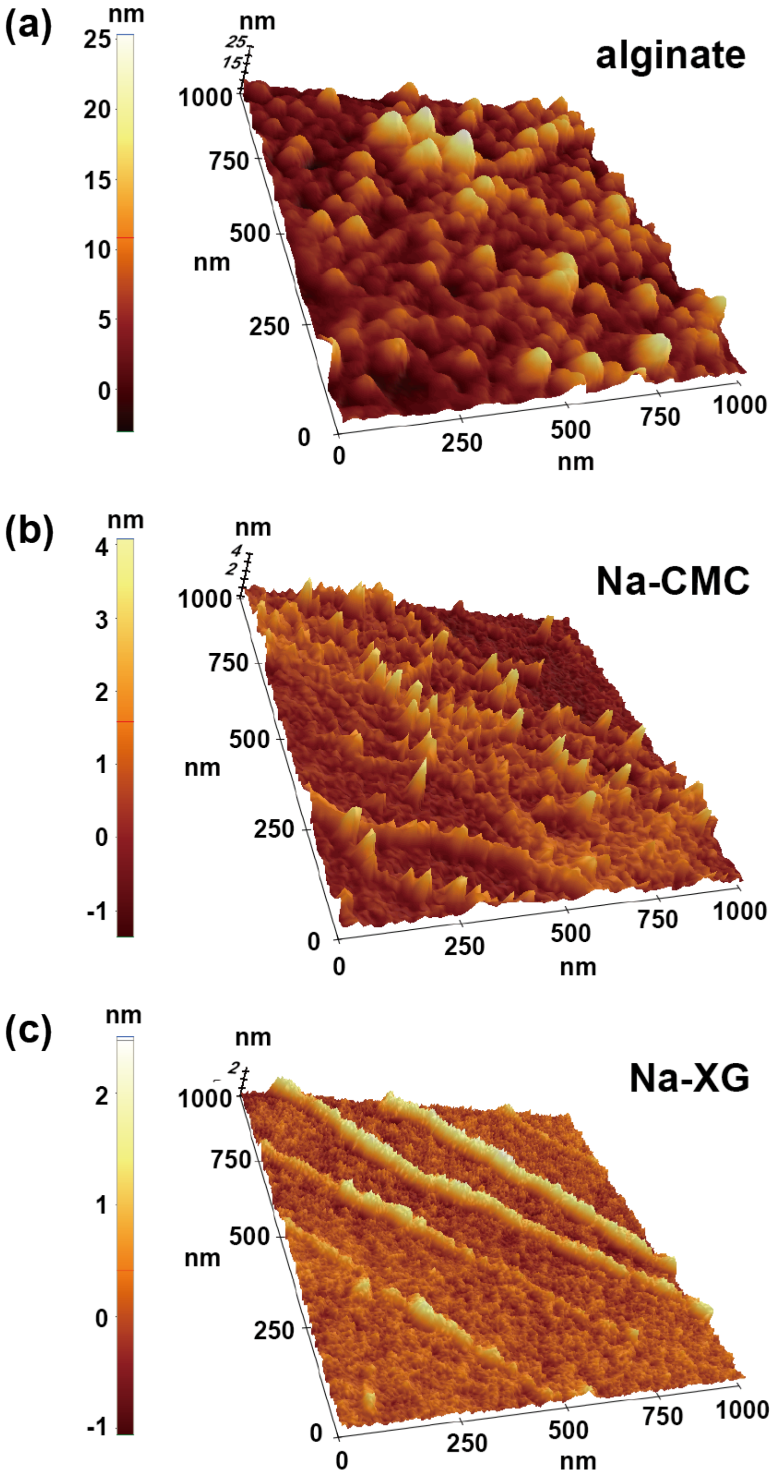


Fig. S3 3D scanning probe microscopy images of (a) alginate (b) Na-CMC, and (c) Na-XG.

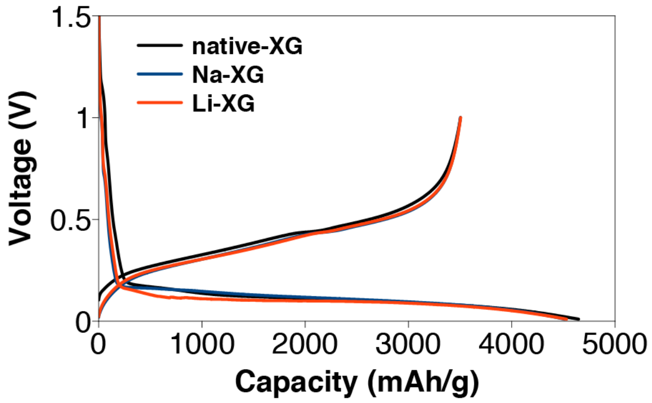


Fig. S4 The 1st voltage profiles of Si/native-XG, Si/Na-XG, and Si/Li-XG at 0.1C (350 mA g^{-1}).

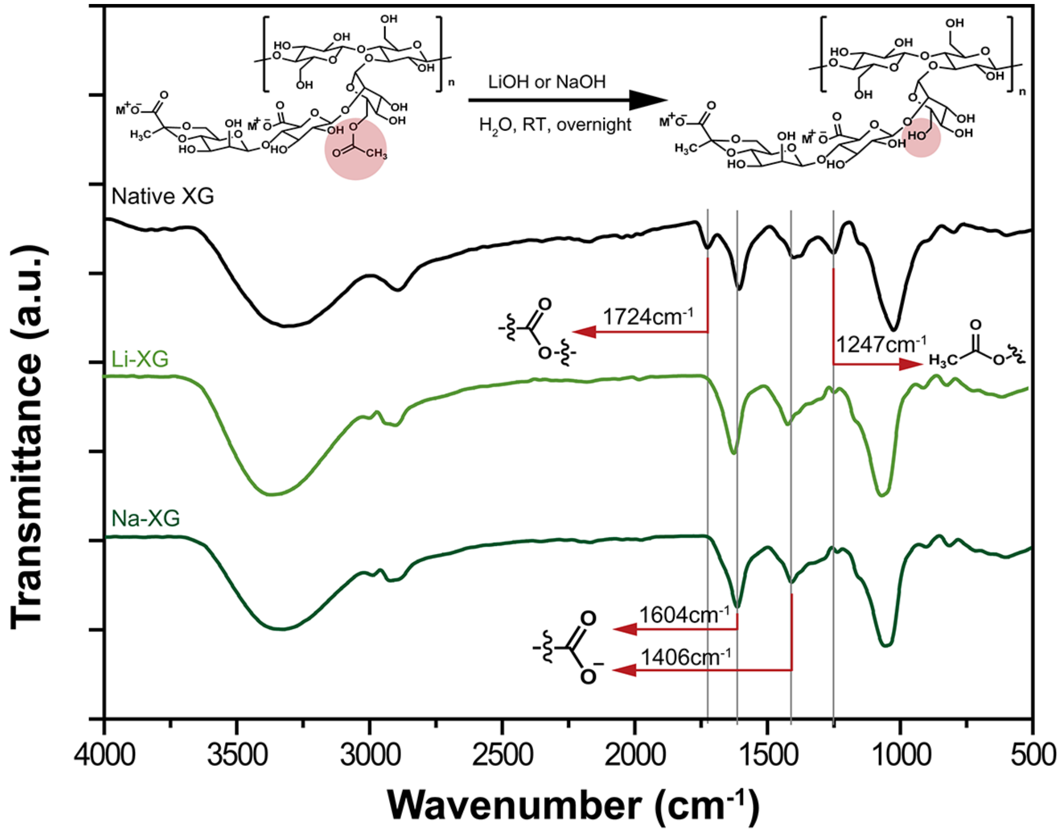


Fig. S5 FTIR spectra of native-XG, Li-XG, and Na-XG. After the hydrolysis of native-XG, the absorption peaks at 1724 cm^{-1} (C=O stretching of acetyl group) and 1247 cm^{-1} (C-O stretching of acetyl group) disappeared, reflecting the quantitative conversion of the acetyl group of native-XG to the hydroxyl group (shaded in red in inset structures).

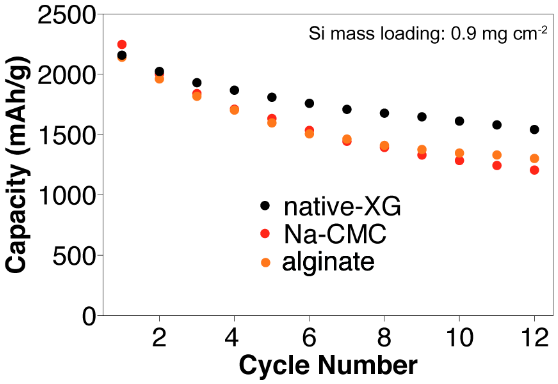


Fig. S6 Cycling performance of the representative Si electrodes with increased Si loadings of 0.9 mg cm^{-2} at 1C (3500 mA g^{-1}) for both charge and discharge in the voltage range of 0.01~1.0 V vs. Li/Li^{+}.

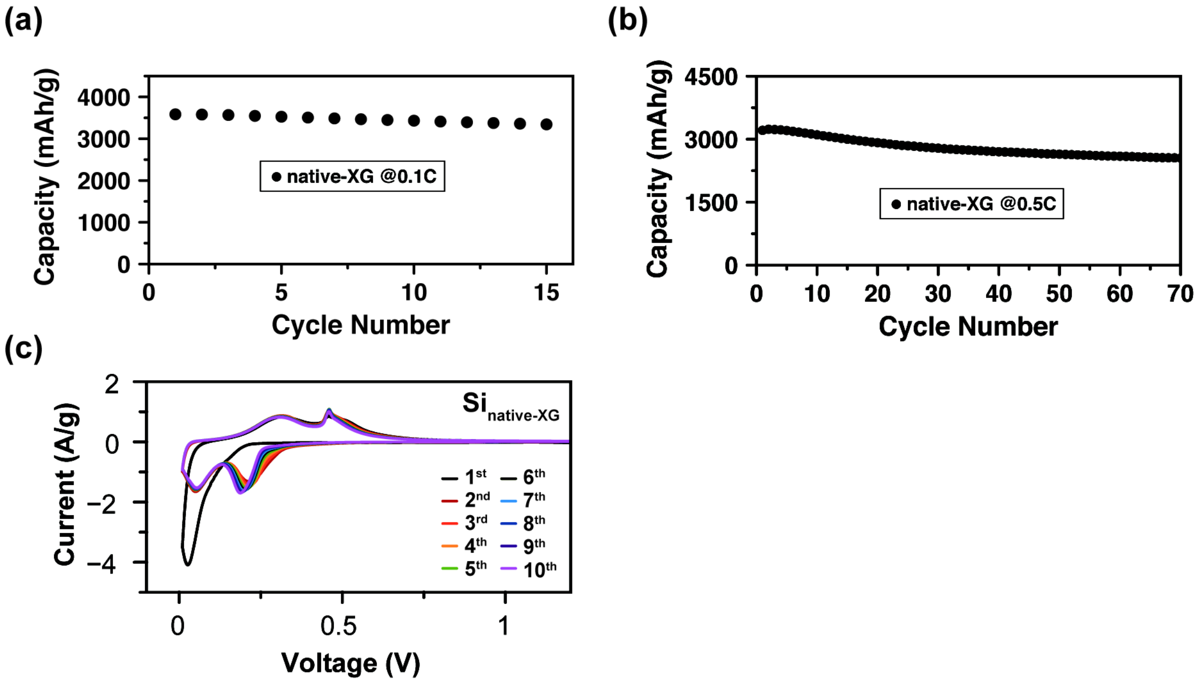


Fig. S7 The cycling performance of Si/native-XG at (a) 0.1C, (b) 0.5C, and (c) CV profiles for the first 10 cycles of Si/native-XG (scan rate =30 μ V s^{-1}). 1C= 3500 mA g^{-1}. The loading of Si = 0.3 mg cm^{-2}.

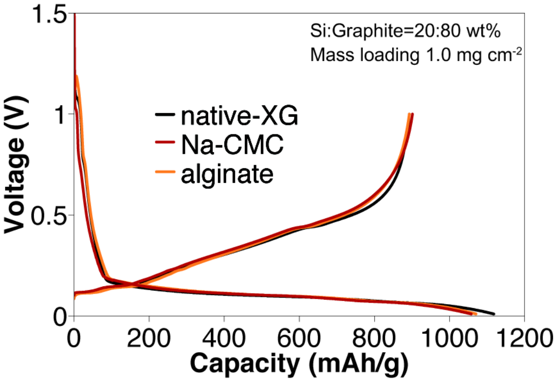


Fig. S8 The first voltage profiles of the Si/graphite composite electrodes based on different binders at 0.1C (98 mA g^{-1}) in the voltage range of 0.01~1.0 V vs. Li/Li^{+}. Active material loading=1.0 mg cm^{-2}.

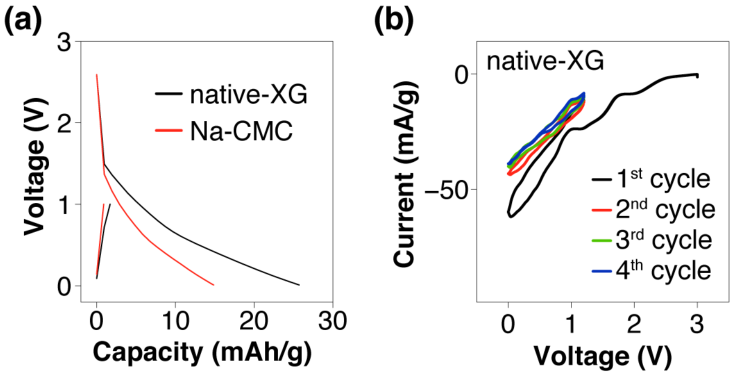


Fig. S9 (a) The voltage profiles of binder-only samples measured at 0.1C (350 mA g^{-1}). (b) Cyclic voltammetry curves of native-XG for the first four cycles showing no redox activity.

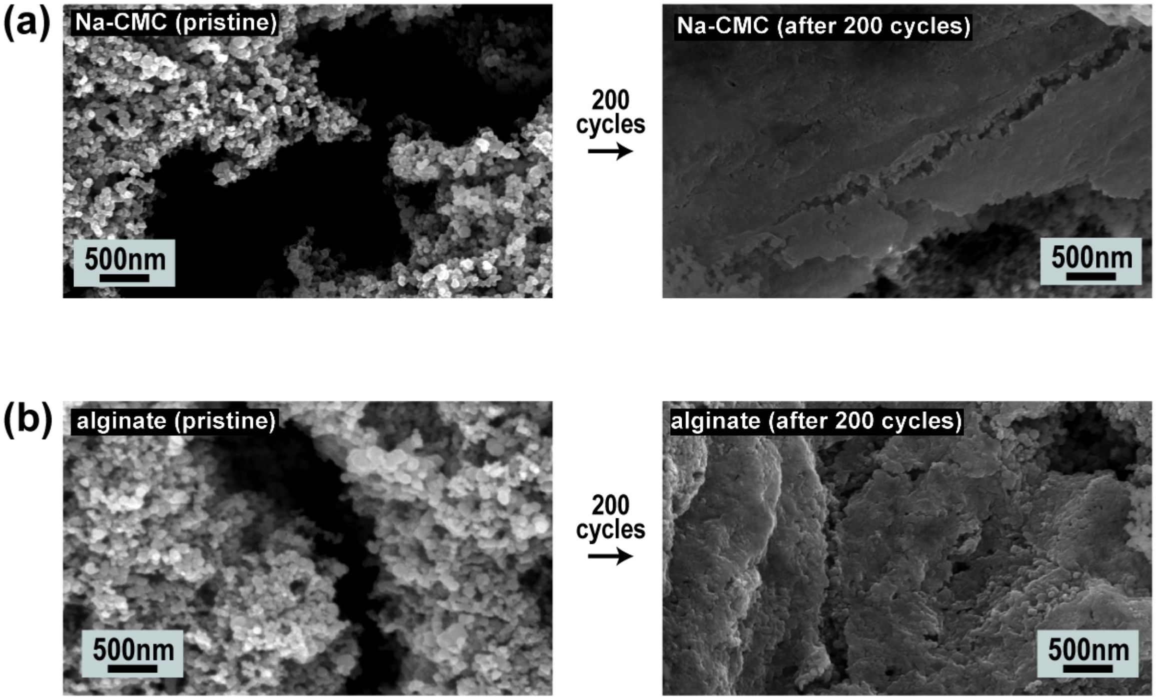


Fig. S10 SEM images of (a) Si/Na-CMC and (b) Si/alginate before and after 200 cycles.