Layer-by-Layer Assembly of Single-charged Ion with Rigid Polyampholyte

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Supporting Information

All reagents were purchased from Aldrich and used without purification except SPES, which was synthesized in our laboratory.[17] Silicon wafers and quartz slides were cleaned in an 80°C piranha solution (H_2SO_4-H_2O_2 (70:30), v/v) for 40 min, rinsed with Milli-Q water, and dried with nitrogen prior to use.

Assembly of SPES with PDDA: The substrate was dipped in the SPES solution (C_2H_5OH-H_2O (3:7), 1mg/mL) for 60min, removed and rinsed with C_2H_5OH-H_2O solvent, and dried with N_2. The substrate was then dipped in the PDDA aqueous solution (1mg/mL) for 40min, rinsed with water and dried with N_2. The deposition cycle was repeated until a desired number of layers was obtained.

Assembly of SPES with $[BMIM]^+$: The substrate was dipped in the SPES solution (C_2H_5OH-H_2O (3:7), 1mg/mL) for 120min, removed and rinsed with C_2H_5OH-H_2O, and dried with N_2. The substrate was then dipped in the [BMIM]Cl aqueous solution (2mg/mL) for 30min, rinsed with water and dried with N_2. The deposition cycle was repeated until a desired number of layers was obtained.

Instrumentation: A homemade quartz crystal microbalance (QCM) was used to detect the mass of the deposited layers using a 9 MHz quartz electrode coated with Ag on both sides. The QCM frequency shifts were monitored with a Protek C3100 universal frequency counter. Atomic force microscopy (AFM) measurements were performed on a SPA300HV microscope equipped with an SPI 3800 controller to investigate the surface morphology of the SPES/$[BMIM]^+$ multilayers. X-ray Photoelectron Spectra (XPS) were obtained on a Thermo Electron ESCALAB 250 spectrometer equipped with a monochromatic Al X-ray source (1486.6eV). The spectra were recorded at a 90° takeoff angle with 20eV pass energy. The sensitivity factors were obtained from standard samples for determination of the atomic concentrations (C 1s, 0.25; N 1s, 0.42; S 2p, 0.54). UV-vis spectra of the thin films deposited on quartz slides were collected on a Shimadzu UV-2450 spectrophotometer.

Figure S1 shows the QCM frequency shifts for the alternating adsorptions of SPES (odd layers) and PDDA (even layers). The average frequency decrease for the deposition of one SPES layer and one PDDA layer was 68±3 Hz and 35±2 Hz respectively.

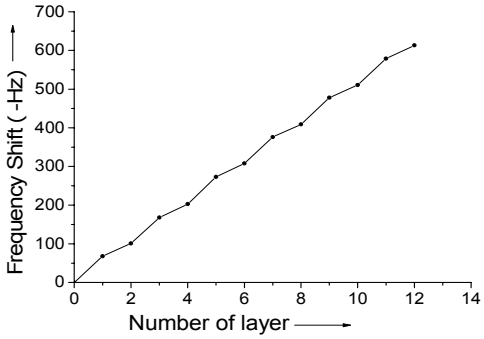

Figure S1. QCM frequency shifts for alternating adsorptions of SPES (odd layers) and PDDA (even layers)

Figure S2 shows the UV-Vis spectra of the SPES/$[BMIM]^+$ multilayers assembled on quartz substrate (primed with 2 PDDA/PSS bilayers) with different number of bilayers. The inset shows the absorptivities at 278 and 204 nm vs the number of bilayers deposited.

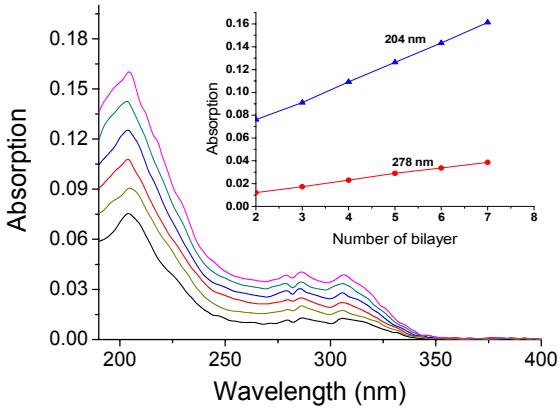

Figure S2. UV-vis spectra of SPES/$[BMIM]^+$ multilayers with different number of bilayers deposited on quartz

The surface morphology of the SPES/$[BMIM]^+$ multilayers was assessed by AFM, and the data is shown in Figure S3.

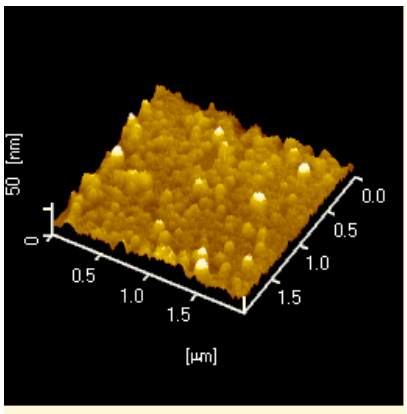

Figure S3. AFM image of SPES/$[BMIM]^+$ multilayers

PSS was attempted to assemble with $[BMIM]^+$, and the process was monitored by UV-Vis spectroscopy. As can be seen in Figure S4, no significant amount of the multilayer growth was detected.

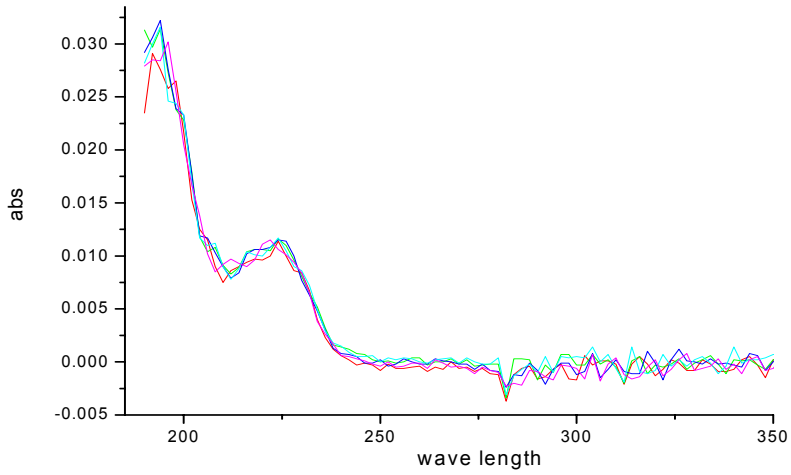

Figure S4. UV-vis spectra of a quartz substrate (primed with 2 PDDA/PSS bilayers) immersed in PSS and $[BMIM]^+$ solutions alternately (30 min each deposition) for up to 5 cycles.