Electronic Supplementary Information

Nanoporous Platinum Solid-State Reference Electrode with Layer-by-Layer Polyelectrolyte Micro-Junction for Microfluidic pH Sensing Chip

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S1. Reagents

All the reagents were prepared using de-ionized (DI) water (NANOpure Diamond, Barnstead), and all the chemicals were used as received without further purification. Diallyldimethylammonium chloride (DADMAC), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photo-initiator), N,N'-methylenebisacrylamide (cross linker), and dimethyl sulphoxide (DMSO) were purchased from Sigma. Poly-dimethylsiloxane (PDMS) Sylgard 184 (Dow-corning), epoxy-type SU-8 (negative PR), and its developer (Microchem) were used to mold the PDMS. Sulfuric acids, hydrogen peroxide, acetone, methanol, and hexamethyldisilazane (HMDS) of CMOS grade were purchased from J. T. Baker to pattern the Au electrodes. AZ5214-E (positive PR) and AZ300MIF (developer) were the products of Clariant (Switzerland). Both PR and HMDS were stored at 4 °C in a refrigerator. Nanoporous Pt (npPt) was electroplated by using tert-octylphenoxypolyethoxyethanol (Triton X-100, Sigma) and hydrogen hexachloroplatinate hydrate (HCPA, Aldrich). NaH_2PO_4(98%), Na_2HPO_4(98%), and KCl(99.5%) from Junsei Chemical (Japan) was employed to prepare phosphate buffered saline (PBS). Sodium tetraborate, boric acid, citric acid, and sodium citrate (Aldrich) were used to prepare borate buffer, citrate buffer. Tris(hydroxymethyl)aminomethane from Bioshop (Canada) was employed for TRIS hydrochloride buffer. Calibration buffers and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were the products of Thermo Scientific (USA) and of Calbiochem (USA), respectively. Minimum Essential Medium Eagle (MEM) and Dulbecco's Modified Eagle's Medium (DMEM) were purchased from Welgene (Korea).

S2. PDMS layer micro-patterning

A slide glass (Corning 2947, 75 mm × 25 mm, 1 mm thick) was cleaned in a piranha solution (H_2SO_4:H_2O_2=3:1) for 1 h, and rinsed with DI water, acetone, methanol, and then DI water (twice). The rinsed slide glass was baked on a hot plate at 150 °C for 10 min to dehydrate the surface, and then it was cooled to room temperature. HMDS was spin-coated by a spin-coater (YS-100MD, Won Corporation) at 4000 rpm for 30 s and the solvent was evaporated on a hot plate at 150 °C for 5 min. SU-8 was spin-coated on the cooled HDMS-coated slide glass at 1800 rpm for 30 s, which resulted in a 50 μm thick SU-8 film, and baked on a hot plate at 65 °C for 2 min and then at 90 °C for 5 min. The cooled SU-8-coated slide glass was exposed to UV light (365 nm, 16 mW cm^{-2}) through a patterned mask for 10 s using a mask aligner (MDE-4000, Midas system), baked at 65°C for 1 min and at 90 °C for 2 min, cooled, and then developed with SU-8 developer for 1 min. The developed slide glass was carefully rinsed with isopropyl alcohol and DI water, and cured on a hot plate at 175 °C for 2 h to facilitate surface adhesion. To prepare the PDMS layer containing channel patterns, the mixture (10:1 in volume) of PDMS polymer base (Sylgard 184A, Dow Corning Corp.) and a curing agent (Sylgard 184B, Dow Corning Corp.) was poured on the master mold, and kept it in a vacuum chamber for 1 h for complete degassing, and then cured for 2 h at 60 °C in an oven. The cured PDMS replica was peeled off from the master mold and perforated at the sampling chamber using a punch.

S3. Au electrode patterning

A slide glass was cleaned and HMDS was coated on it as previously described[1]. The HMDS-coated slide glass (2000 rpm, 30 s) was spin-coated with positive PR (AZ5214-E), baked (100 °C, 1 min), exposed to UV light (365 nm, 16 mW cm-2, 5 s) using an mask of the electrode pattern, and then baked (100 °C, 5 min) again. For image reversal process, PR on the slide glass was illuminated by UV for 15 s, developed with AZ300MIF (1 min), rinsed with DI water, and dried by air-blowing. Ti (20 nm) and Au layers (100 nm) were sequentially deposited by a thermal evaporator (ALPS-C03, Alpha-Plus), and the developed PR was soaked into acetone and lifted off by ultrasonic cleaning (5 min) in ultra sonic cleaner (3510E-DTH, Bransonic).

S4. Electrodeposition of npPt

The slide glass with Au electrode pattern was insulated with a polyimide tape except two circular areas (diameter 2 mm) for npPt electrodes to be formed. The npPt was electroplated on Au by following the protocol described in our previous work[2] with some modification. In brief, an electroplating bath was filled with the mixture of Triton X-100 (50 wt %), 0.3 M NaCl aqueous solution (45 wt %), and hexachloroplatinic acid (HCPA; 5wt %) at 40 °C.

Then the insulated Au electrode pattern was inserted into the electroplating solution with Ag|AgCl (3M KCl) reference electrode and Pt wire counter electrode. The npPt was electrochemically deposited on exposed Au pattern by applying –0.2 V vs. Ag|AgCl. The npPt film as made was denoted by L_2-ePt in the previous report[2]. The real surface area of npPt was determined from the charge corresponding to cathodic adsorption of hydrogen in cyclic voltammogram (1 M H_2SO_4, scan rate, 0.2 V s^{-1}), using a conversion factor of 210 μ C cm^{-2}.[3] To form an oxide layer on Pt, npPt was electrochemically oxidized by applying +0.6 V versus Ag|AgCl in PBS (pH 7.4) for 500 s. But this process is not mandatory because npPt itself has oxide surface at ambient condition, and so the npPt with oxidized surface will be denoted as npPt indifferently. Bare npPt and npPt coated with polyphenol (PPh/npPt) were tested as pH-IE. Polyphenol layer was electrochemically polymerized on npPt by cycling potential five times between +0.2 and +1.0 V versus Ag|AgCl (3 M KCl) at 2 mV s^{-1} in PBS (pH 7.4) containing 10 mM phenol[4].

S5. Polyelectrolyte (PE) fabrication

PE junction was single-layered PDADMAC or PDADMAC-co-AMPSA or multi-layered LBL-PE, which was polymerized by (repeated) photo polymerization of the corresponding polymerization solution in the microchannel and PE chamber. The solution for PDADMAC polymerization was prepared by diluting 9.95 ml of DADMAC aqueous solution (65 wt%) with 10 ml of DI water and mixing 0.26 g of photo-initiator and 6.7 ml of cross linker solution (20 wt% in DMSO). To prepare PDADMAC impregnating PBS of pH 2.2, 7.2, or 12.0 ($PDADMAC_{PBS(2.2)}$, $PDADMAC_{PBS(7.2)}$, and $PDADMAC_{PBS(12.0)}$, respectively), 10 ml of corresponding PBS was used instead of 10 ml of DI water. The solution for PAMSA polymerization was prepared by dissolving 8.25 g of AMPSA in 20 ml of DI water and mixing 0.26 g of photo-initiator and 6.7 ml of cross linker solution (20 wt% in DMSO). The solution for PDADMAC-co-PAMPSA polymerization was prepared by diluting 9.95 ml of DADMAC (65 wt%) with 30 ml of DI water and mixing 8.25 g of AMPSA and 0.52 g of photo-initiator and 13.4 ml of cross linker solution (20 wt% in DMSO). After finishing the polymerization processes, the PE was cleaned with 1 M KCl solution, DI water, and PBS solution.

The photo polymerization processes of PDADMAC and PAMPSA were repeated to obtain the LBL structure as shown in Figure 1D. To inject corresponding solution for polymerization of the respective layer, two syringe needles were inserted through the flexible PDMS. For the first polyelectrolyte (PE) plug, one needle through the PDMS cover was used as an outlet for air while the other was placed at the end of microchannel or reservoir to deliver the solution for polymerization. Photo polymerization was carried out by exposing the injected solution to UV light through photo-mask, and then the residues were removed by sucking out the solution and refilling with de-ionized water. A few times repetition of rinsing made the microchannel clean. For the second PE plug, the microchannel was filled with the corresponding solution and the photo polymerization process was repeated. After constructing all the LBL PE plugs, the needle through the PDMS cover layer to air was taken out and the aperture were sealed with silicon rubber paste.

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