Electronic Supplementary Information (ESI)

## Microcontact electrochemical etching technique for rapid fabrication of glass-based microfluidic chips

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## **ESI-1.** Agarose Mold Fabrication

Considering that the stamp for  $\mu$ CECE should be obtained easily and adsorbed mass electrolyte, the high-strength agarose was selected for the stamp material. The preparation of micropatterned high-strength agarose (American AMRESCO, biotechnology grade) is described in detail elsewhere [L. Zhang, J.L. Zhuang, X.Z Ma, J. Tang, Z.W. Tian, *Electrochem. Commun.*, 2007, **9**, 2529-2533.]. The master used here was a Si wafer with microstructures fabricated by Inductively Coupled Plasma (ICP). After stripping from the master, micropatterned stamp was soaked in the electrolyte solution containing 0.2mol·L<sup>-1</sup> KCl for 2h. Prior to use, the gels were dried on filter paper for 10min and streamed under N<sub>2</sub> for 100s.

The fabrication procedure was as follows (Fig. S1): a Si master with desirable channels (50µm wide, 17µm deep) was obtained by conventional lithography using ICP, then a hot degassed agarose solution (8-12wt%) was cast against the Si master with depressions embossed on its surface. After cooling and peeling, the agarose gel with a negative copy was obtained, the average width and height of protuberant structure are 48µm and 17µm respectively. The fabrication process starting from the Si master costs about 15 min and the agarose stamp is re-usable in the process of µCECE. It should be noted that edge of the protuberant structure is collapsed(Fig. S2), probably due to a capillary effect when the stamp was dried in the air. This issue generated the lateral deviation of the fabricated ridges from those on the Si master, and the deviation is approximately  $(50-48)/2/48 \times 100\%=2.6\%$ .



Fig. S1. Schematic illustration of the process for fabrication of agarose mold.



Fig. S2. Top view and cross-sectional profile (insert) of agarose stamp.

## ESI-2. Structure of glass-based microchip and Electrophoresis conditions

The structure of the cross chip is 45mm from injection cross to the outlet and 5mm from injection junction to inlet and sample and sample waste respectively(Fig. S3-a). The detection point was located at a separation distance of 10mm. All channels were typically 102µm wide and 25µm deep (Fig. S3-b).



Fig. S3. Optical image of (a) cross chip and (b) cross-sectional profile of microchannel.

The composition of the electrolyte systems used in this work was presented in Table S1. All reagents were of analytical grade. An in-house built single-point LIF detection system based on an inverted fluorescence microscope (Motic AE31, Motic Incorporation Ltd, HongKong) equipped with a PMT detector (CR125, Hamamatsu Photonics China Co. Ltd) was used for the detection of the microfluidic devices (Fig. S4).

The optimum voltages and times were: sampling, 400V (400V/cm) for 20s; separation, 1500V (320V/cm) for up to 30s.

Electrolyte	Composition
Borate buffer solution 10mM pH 9.2	FITC 10 μM

Table S1. Composition of the electrolyte systems



Fig. S4. Schematic of the instrumentation setup used for microfluidic devices.