

## **Ion Current Oscillation of Polyelectrolyte Modified Micropipettes**

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## S1. Experimental Section

**1. Chemicals and Solutions.** 1-Vinylimidazole (Vim), 2-bromoisobutyryl bromide (BiBBr), 3-aminopropyl- triethoxysilane (ATPES), copper (I) bromide (CuBr, 98%), triethylamine (TEA, 99%) and N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from J&K Chemical (Tianjin, China), Other chemicals were of at least analytical grade reagents and used as received. All aqueous solutions were prepared with Milli-Q water.

**2. Apparatus and Instruments.** The micropipettes were fabricated by a CO<sub>2</sub>-laser-based pipet puller (P-2000, Sutter Instrument Co.) with borosilicate glass capillaries (1.50 mm O.D. and 0.86 mm I.D., without filament), then the pipettes were polished to 10 μm under MF-900 microgrinder (Narishige International USA, Inc.). Current-voltage (*I-V*) curves and Current-time (*I-t*) curves were recorded by using a Keithely 2636B SourceMeter (Tektronix Co. U.S.A.). The potential was applied to the modified micropipettes by using two Ag/AgCl electrodes to avoid the influence of Faraday processes: one was inserted into the pipette and the other one was placed in the external electrolyte environment, acting as reference electrode. The potential given herein were  $E_{\text{internal}}$  vs  $E_{\text{external}}$ .

### 3. Preparation of PimB modified micropipette

#### 3.1 Synthesis of BTPAm silane initiator.

Synthesis of 2-bromo-2-methyl-N-(3-(triethoxysilyl) propanamide) (BTPAm) silane initiator was performed according to a previous report<sup>1</sup>. Two mixed solutions were prepared according to the following formula:

Solution A: TEA (0.12 mL, 0.8 mmol), ATPES (0.18 mL, 0.8 mmol), dissolved in 10 mL dried toluene.

Solution B: BiBBr (0.1 mL, 0.8 mmol), dissolved in 10 mL dried toluene.

Solution B was added to a stirred solution A dropwise under 0 °C for 2h under nitrogen. Then the mixed solution was warmed to room temperature and stirred for 24h. Then mixture was filtered by a filter paper to remove the by-product insoluble substances. Evaporate the filtrate to remove the unreacted TEA and solvent under reduced pressure, the was evaporated to remove the unreacted TEA under reduced pressure. The resulting product, BTPAm, was yellowish thick liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.60 (m, 2H), 1.20 (t, 9H), 1.65 (m, 2H), 1.95, (s, 6H), 3.25 (m, 2H), 3.80 (m, 6H).

#### 3.2 Functionalization of the micropipettes

The preparation of PvimB modified micropipettes were conducted with a previous reported method. Briefly, borosilicate glass capillaries were pretreated by piranha solution (30% H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> = 3:7) and standard clean solution (30% H<sub>2</sub>O<sub>2</sub>/NH<sub>4</sub>OH/H<sub>2</sub>O = 1:1:5) successively. Then dried and clean capillaries were pulled by the laser puller (The detailed parameters were listed in Table S1) to get a 3- $\mu$ m-diameter conical microchannel. All the fabricated micropipettes were checked by an optical microscope to ensure the consistence of the cone angle and the pore size.

Then the micropipettes were backfilled with BTPAm solution (5%, v/v in acetonitrile), and placed in pure acetonitrile atmosphere overnight. After a thorough and successively wash of acetonitrile, ethanol and water, initiator-modified micropipettes were obtained.

Before the polymerization, the initiator-modified micropipettes were backfilled with a solution containing 28 mg/mL Vim and 17mg/mL PMDETA (solved in water) which was degassed for 15 min under nitrogen atmosphere. Then tips of the fulfilled pipettes were immersed in the mixed solution of Vim, PMDETA and 3.5 mg/mL CuBr, the resulting mixture was degassed for a further 15 min and was kept under nitrogen atmosphere. Polymerization started when the reactor was immersed into an oil bath of 65 °C, and stopped after 24 h when the vessel was removed and cool down to room temperature.

**Table S1.** Detailed parameters of the Laser puller, relevant parameters require further adjustments owing to the characteristic differences of the instruments.

Cycles	Heat	Filament	Velocity	Delay	Pull
1	405	4	28	128	10
2	425	5	30	128	10

## S2. Derivation of the Ion Current Changes in ICO

The whole modified pipette could be regarded as a hollow truncated cone structure whose tip radius, effective length and half-cone angle are  $R$ ,  $L$  and  $\theta$  respectively. Polyimidazole layer was modified to the inner surface of the pipette and  $b$  is the thickness of Polyimidazole layer. In asymmetric solution, part of the pipette was in acidic environment and protonated, and  $a$  is the length of this section. While the rest of the pipette was in alkaline environment, and the length of this deprotonated section is  $(L-a)$  (Figure S1A). Therefore, based on previous understanding to the ion transport theories, a simplified equivalent circuit could be given in Figure S1B: The modified pipette could be regarded as the parallel connection of bulk solution and surface section. In the asymmetric solution environment, the conductivity difference of PBS with different pH is ignorable since the ionic strength difference is ignorable, meanwhile the majority of ion concentration changes was in the surface layer, in this case the conductivity of bulk solution in the micropipette ( $R_{bulk}$  in Figure S1B) could be written as a constant which is related to the geometry and the ionic strength:

$$G_{bulk} = \int_0^L \frac{F \sum |z_i| c_i \mu_i dx}{\pi(R + x \tan \theta)^2} dx \# Eq.1$$

Considering a modified micropipette under constant negative bias voltage, the surface conductivity is formed by the highly conductive deprotonated section ( $R_{surf, Vim}$  in Figure S1B) and the low conductive protonated state ( $R_{surf, VimH+}$  in Figure S1B), in this case the conductivity could be written as the following formula

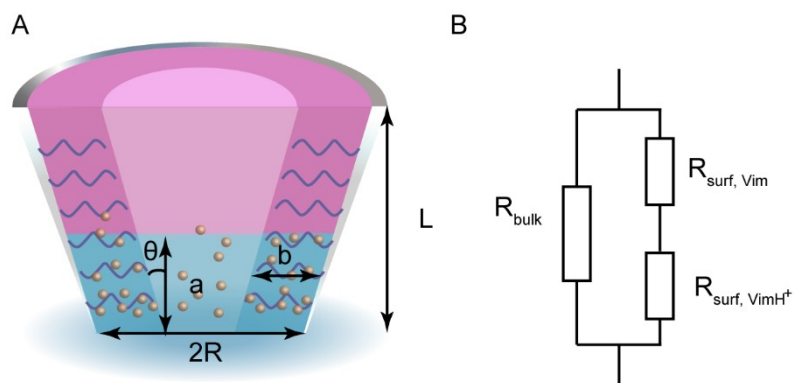
$$G_{surf} = \int_0^L G_{surf}(x) dx = \int_0^a \frac{F \sum_{i,+} |z_i| c_i \mu_i dx}{2\pi(R + x \tan \theta)b} dx + \int_a^L \frac{F \sum_{i,-} |z_i| c_i \mu_i dx}{2\pi(R + x \tan \theta)b} dx \# Eq.2$$

In this case the ion current through the modified micropipette could be given according to ohm's law:

$$I = E(G_{bulk} + G_{surf}) \# Eq.3$$

Considering the ion transport theories in previous reports<sup>2, 3</sup>, it could be noticed that the total ion current is related to the bias voltage  $E$ , the ion distribution in the polyimidazole layer  $c_i(x)$  and the movement and the changes on the protonation/deprotonation section (i.e. changes of  $a$ ). Under fixed bias voltage and fixed pH gradient, current  $I$  is the monovalent function of  $a$ , in this case an oscillating ion current could be observed with  $a$  change periodically. Furthermore, considering ICO observation in difference conditions, changes on pH gradient contributed to the changes of surface chemistry, in this case the high conductivity/low conductivity state difference was regulated, resulting in the changes on the ICO phenomena; Besides, with the changes of  $E$ , not only Eq. 3 was directly regulated by the electrical field

changes, but also  $c_i(x)$  was changed owing to the changes on the accumulation/depletion level, in this case the ICO behavior could be manipulated by the pH gradient and bias voltages.



**Figure S1.** (A) Phenomenological model for a PvimB modified micropipette in asymmetric solution. (B) Equivalent circuit for a PvimB modified micropipette in asymmetric solution.

1. X. He, K. Zhang, T. Li, Y. Jiang, P. Yu and L. Mao, *Journal of the American Chemical Society*, 2017, **139**, 1396-1399.
2. A. R. Poggioli, A. Siria and L. Bocquet, *Journal of Physical Chemistry B*, 2019, **123**, 1171-1185.
3. X. He, K. Zhang, Y. Liu, F. Wu, P. Yu and L. Mao, *Angewandte Chemie International Edition*, 2018, **57**, 4590-4593.