Electronic Supplementary Information (ESI)

Probing the structure of a water/nitrobenzene interface by scanning ion conductance microscopy

Tianrong Ji, Zhongwei Liang, Xinyu Zhu, Lingyu Wang, Shujuan Liu and Yuanhua Shao*

Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

*E-mail: yhshao@pku.edu.cn

Table of Contents

I. Modification of the Instrument .................................................. S2
II. Scanning Electron Microscopy of the nanopipette .......................... S3
III. Approach Curves of different scan rates ...................................... S4
IV. The effect of charging current .................................................... S6
V. References ................................................................................. S7
I. Modification of the instrument

Scanning ion conductance microscopy (SICM) is one of the scanning probe microscopies with high spatial resolution. By utilizing a nanopipette filled with an electrolyte solution as a probe, SICM has been widely employed for imaging living cells under physiological conditions, controlled delivery of biological molecules and combination with other techniques. For most applications of SICM, a vertical approach step of 1 nm is enough. However, to investigate the thickness of liquid/liquid interfaces which is usually less than 1 nm, a smaller approach step is needed. As a result, our system has been modified to approach 0.1 nm each step on z direction by the Ionscope Company.

Technically, a 0.1 nm approach step is supported by the delicate instrument with stable and precise scanning systems. The scan head consists of a PIHera P-621.ZCL and a PIHera P-621.1CL stage with 100 × 100 μm travel range (Physik Instrumente (PI), Germany) for X and Y direction nanopositioning, respectively. For the pipette positioning along Z direction, a high-performance LISA piezo actuator P-753.21C (PI) with travel range of 25 μm is applied. The closed-loop/open-loop resolution of this actuator is 0.1 nm (see the Datasheet for P-753 LISA Linear Actuator & Stage).

To actually achieve the approach step of 0.1 nm, some modification has been made on the software. The z direction DAC board has 2^16 bits, i.e., 65536 bits to resolve 25 μm, which is the original travel range of the pipette in z direction. Herein, the travel range has been reduced to 6.55 μm (0.1 nm multiplied by 65536) by decreasing the voltage inputted into the PI amplifier. The piezo stage was originally designed to travel 25 μm driven by a voltage of 10 V. According to this linearity, the voltage on our system was reduced to 2.62 V to travel 6.55 μm.

Furthermore, to avoid the mechanical vibration, electromagnetic interference and thermal effect, the electrochemical cell was mounted on a vibration isolation table (Technical Manufacturing Corporation, U.S.A) and shielded in a Faraday cage (maintaining the thermal stability), and the setup is installed at the ground floor. In addition, the stability of input voltage has been evaluated by an oscilloscope.
(Tektronix 2022B 200 MHz, U.S.A). Results showed that the electronic noise was too low to be detected. There was no significant difference between the noise of oscilloscope itself and the noise of input signal, and even this low-level noise would be further filtered out by the PI amplifier to achieve the precise control of piezo stage.

To sum up, based on the delicate hardware and modified software, our system has the capability to approach 0.1 nm each step vertically, and probe the structure of a W/Nb interface at sub-nanometer scale.

II. Scanning Electron Microscopy of the nanopipettes

The nanopipettes used in this work had a small orifice radius less than 10 nm. Electrochemical characterization showed that the effective inner radius was about 3.5 nm, which was confirmed by the parallel SEM characterization from the side view. Since the glass nanopipettes are nonconductive in nature, it is usually very hard to characterize them by SEM. In order to do so, one has to coat some conductive layers (such as carbon or gold) on the nanopipettes. However, it is quite difficult to obtain a clear SEM image from the top view when the pipette is at this size. As shown in Fig. S1, the inner radius of the nanopipette can be estimated to be about 5 to 6 nm, although not very precisely.

![Fig. S1 Top view SEM image of a nanopipette.](image)

Due to the thin layer coating and low atomic number of carbon, the coating is relatively easy for the electron to transmit. As a result, the carbon coating on the edge
of the pipette profile seems semi-transparent (see Fig. S2). Luckily, from this feature, we can estimate that the thickness of carbon coating although it is not quite uniform at different part of the tip, and therefore, the cone angle is measured from the surface of the pipette, excluding the interference of the carbon coating. The result indicates a half-cone angle \( \theta/2 \) of approximately 6°, in good agreement with the value obtained from micropipettes by Amemiya\(^5\) and Kakiuchi\(^6\).

![Fig. S2 SEM image showing the cone angle of the nanapipette.](image)

**III. Approach Curves of different scan rates**

The shape of the approach curves is correlated with the structure of the electrical double layer. To study how much kinetics affects the curves, we have obtained a family of SICM approach curves with various scan rates (see Fig. S3), and analyzed their characteristic (see Table S1).

Before the tip touches the interface, it has been in the NB phase for a long time to reach the steady state of ion transfer across the interface driven by the external applied potential. As a result, the organic specific distance listed in Table S1 barely changes with five different scan rates. While the tip is penetrating the interface, a dramatic current change happens, from which the thickness of the interface can be estimated. If the tip scans fast enough compared to the dynamic change of the solutions, the tip will pass through the interface in an instant, during which the interface can be considered as static. Consequently, the interfacial thickness at various scan rates has no
significant change (except the one at 1000 nm/s as discussed below). After the pipette traverses the interface, the tip current is in inverse proportion to the concentration of Cl\(^-\) in the aqueous diffuse layer. As shown in Table S1, the aqueous specific distance almost keeps at a constant level when the scan rate is 333, 150 and 50 nm/s, but increases 0.5 and 2 times at the rate of 500 and 1000 nm/s, respectively. This result probably indicates that the maximum scan rate the system can withstand is approximately 333 nm/s, under which the information extracted from the approach curves is reliable. A faster scan rate of 500 or 1000 nm/s may bring much mechanical disturbance to the interface, resulting in the relatively larger aqueous specific distance and interfacial thickness. To avoid this disturbance, the tip should approach as slow as possible. However, if the scan rate is too slow, it would take a very long time to finish an approach curve, and the change of the environment, the volatilization of the solution and the shift of the interface due to the volatilization cannot be neglected. Given all the factors discussed above, a moderate scan rate of 50 nm/s was selected as a standard condition.

**Fig. S3** SICM approach curves obtained with different scan rates. The concentration of LiCl in the bottom aqueous phase and the pipette was 10 mM, and the concentration of TPAsTPB in NB was 1 mM. The scan rate was (1) 1000, (2) 500
(moved down 0.30 nA), (3) 333 (moved down 0.75 nA), (4) 150 (moved down 1.20 nA), (5) 50 (moved down 1.35 nA) nm/s. The tip potential was -0.6 V vs. Ag/AgCl.

**Table S1** Characteristics of the approach curves at different scan rates

<table>
<thead>
<tr>
<th>Characteristics of the approach curves</th>
<th>Scan rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000 500 333 150 50</td>
</tr>
<tr>
<td>Aqueous specific distance (nm)</td>
<td>7.1 3.6 2.6 2.2 2.5</td>
</tr>
<tr>
<td>The thickness of the interface (nm)</td>
<td>1.1 0.7 0.4 0.6 0.7</td>
</tr>
<tr>
<td>Organic specific distance (nm)</td>
<td>0.1 0.1 0.1 0.0 0.2</td>
</tr>
</tbody>
</table>

**IV. The effect of charging current**

The tip current at negative z coordinate in the approach curves consisted of both Faraday current and charging current. To investigate how much the charging current affects the experiments, we need to estimate its value.

When the pipette just made contact with the millimeter-sized interface, the charging process mainly occurred within the region of a three dimensional diffusion field of the tip. According to the work of Henry White et al., the thickness of diffusion layer for a nanometer-sized electrode is at the scale of \((6Dt)^{1/2}\), where \(D\) is the diffusion coefficient and \(t\) stands for the time. Due to the smaller size of Cl\(^-\) than TPAs\(^+\), Cl\(^-\) has a larger value of \(D\), which is chosen to estimate the scale of diffusion field. However, since there is no report about \(D\) for Cl\(^-\) in nitrobenzene, we evaluated it to be approximately \(1.8 \times 10^{-6} \text{ cm}^2/\text{s}\) based on \(D\) for Cl\(^-\) in 1,2-dichloroethane \((4.2 \times 10^{-6} \text{ cm}^2/\text{s})\) and the Stocks-Einstein Equation, \(D=kT/6\pi\eta r\) (where \(r\) is the radius of the ion and \(\eta\) is the viscosity of the solvent, 0.779 and 1.863 mPa s for DCE and NB at 25°C, respectively). With the value of \(D\) and \(t\) (around 0.02 s), the thickness of diffusion layer was approximately 4.6 \(\mu\)m.

For simplification, a micropipette with an orifice radius about 4.6 \(\mu\)m was employed to estimate the value of charging current. Fig. S4 shows a cyclic voltammogram obtained at the interface supported by the micropipette between nitrobenzene containing 1 mM TPAsTPB and aqueous solution with 10 mM LiCl. The charging current within the potential window was about 20 pA (see inset in Fig. S4), while the faraday current was at nA level. Consequently, we can have the
conclusion that the effect of charging current was insignificant.

![Cyclic voltammogram](image)

Fig. S4 Cyclic voltammogram obtained at the interface: 1 mM TPAsTPB(NB) || 10 mM LiCl(W). The sweep rate was 100 mV/s. The inset shows the charging current within the potential window (from 100 mV to 300 mV). The black line and the red line correspond to forward scan and reverse scan, respectively.

V. References