Generation and *In Situ* Electrochemical Detection of Transient Nanobubbles

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Figure S1 shows still images of the experimental setup employed in the Coulter counting of transient nanobubbles. The left image shows the piston like emitter (PLE), the reflector (R), cluster (C) at the tip of the PLE, the glass nanopore (GNP), surface confined bubbles (SB) and a bubble (B) on the body of the GNP. This bubble was left behind after the ultrasonic source (the PLE) was terminated (see right image).

Figure S1. Images of the experimental setup deployed in the experiments. PLE is the piston like emitter, R the glass reflector, SB are surface confined bubbles, B the residual bubble, C the cluster and GNP the glass nanopores. The PLE was 2.5 ± 0.1 mm from the surface of the reflector. The GNP edge was 1.8 ± 0.1 mm from the PLE. A bubble (B) left on the outside of the capillary used to make the GNP is also highlighted. The scale bar represents 1 mm.

Movie S1 shows the bubble activity imaged at 20 kfps under these conditions. This shows the bubble activity (at 18 W_{rms}) and their termination as the PLE is allowed to ring down.

Figure S2a shows a schematic representation of the flow and activity that was observed in this system. Figure S2b shows an illustration of the suggested fragmentation of the surface bubbles to produce the transient nanobubbles detected as signals in the ion current.
Figure S2a. Illustration of the bubble activity in the cell employed. Flow, seen by motion in the high-speed imaging, surface confined bubbles and the position of the GNP are illustrated. S2b is an illustration of the suggested fragmentation of an oscillating bubble close to the mouth of the GNP which leads to the production of transient nanobubbles which may translocate.

Figure S3 shows the frequency components present in the current time data acquired for the PLE operating at a reported power of 2 W\textsubscript{rms}. This shows frequency components in each translocation (including \textit{i}(dc) as the 0 Hz component) and a small \textasciitilde 23 kHz noise signal expected for the PLE.
Figure S3 (a) Plot showing the dc component in the current time data. This is essentially the data filtered to be a time average over the analysis window (2 ms). (b) Plot showing the time dependence of the frequency components detected in the current time data for the 440 nm diameter GNP exposed to ultrasound. The PLE was operated at 2 W_{rms}. The aerobic solution contained 10 mM KCl. The colour scale bar is in pA. Note the fundamental frequency of the PLE (~23 kHz) is shown with the annotation ‘f’.

The approach adopted for the instrumentation follows that outlined in the literature\(^1\). A high gain current follower (10\(^9\) V A\(^{-1}\)) was constructed. The signal from this was added to its differential to improve the temporal response of the system. A low pass filter was also added to reduce high frequency noise.

The response of the instrumentation (including the filter) was tested by performing a voltage step across a dummy cell (1 GΩ). Figure S4 shows the response of the instrumentation under these conditions compared to a typical nanobubble event. The step response indicates that the instrument responds rapidly with an initial rise to 90% within 500 µs. The rise rate was measured at a maximum value (e.g. the initial part of the step) at > 2300 pA ms\(^{-1}\). This is greater than the rise time for the bubble translocation of ~ 1400 pA ms\(^{-1}\). These measurements support the conclusion that the nanobubble translocations (see main paper) are not significantly perturbed by the instrumentation.
Figure S4 (a) Plots showing the response of the instrumentation employed as a voltage step (▬) was applied to a 1 GΩ dummy cell. The current response (▬) is shown and can be compared to the response detected for the nanopore for a nanobubble translocation (see (b), ▬).

To characterize the glass nanopores, two experiments were performed. First, voltammetry in Ru(NH₃)₆³⁺ was carried out to determine the diameter of the nanoelectrode template. This allowed for an estimation of the pore mouth dimensions. Second, the uncompensated resistance of the GNP was determined, after the W had been removed by chemical etching, to enable an accurate estimation of the cone angle to be determined. The resistance, $R$, of the GNP² is noted to be related to the cone angle, $\phi$ and the electrolyte conductivity, $\kappa$ in equation 1 where $r$ is the pore radius.
\[ r = \left( \frac{1}{\pi \kappa R} \right) \left[ \frac{1}{\tan \phi} + \left( \frac{\pi}{4} \right) \right] \]  \quad (1) \]

Propagation of errors results in the error in \( r \), \( \delta r \), to be related to the errors in \( R \) and \( \phi \) through equation 2.

\[
\delta r = \left\{ \left( \frac{-\alpha \delta R}{\pi \kappa R^2} \right)^2 + \left( \frac{-\beta \delta \phi}{\sin^2 \phi} \right)^2 \right\}^{1/2} \quad (2)
\]

where

\[
\alpha = \left[ \frac{1}{\tan \phi} + \left( \frac{\pi}{4} \right) \right] \quad (3)
\]

\[
\beta = \left( \frac{1}{\pi \kappa R} \right) \quad (4)
\]

Figure S5 shows the predicted radius of a GNP as a function of the cone angle for a particular pore resistance \( R \).

Figure S5. Plot showing the predicted radius, \( r \), for a known pore resistance, \( R \), of 70 MΩ. The error calculations assumed an error in \( R \) of ± 5% and an error in the cone angle \( \phi \) of ± 0.5°. The calculations were based on the conductivity for 10 mM KCl at 25 °C. Note that the error in \( r \) becomes significant below a cone angle of ~ 6°.
Figure S5 shows that at low cone angles, the uncertainty in the predicted pore radius is high and any calculation would be prone to inaccuracies. Hence, we based our cone angle estimations on the resistance of the pore in combination with the pore dimensions which were inferred from the steady state voltammetry of the template W nanoelectrode prior to chemical etching.

Using the resistance of the pore employed in the study of transient nanobubbles, a half cone angle of 9.58° can be calculated. This can then be used in combination with a COMSOL model to estimate the size of the transient expected for a particular translocation event. Figure S6 shows the maximum change in the current as a function of the bubble radius employed. Included on the figure is an estimate of the minimum event size detectable assuming that a signal to noise ratio of 2 is required and that the noise on the data is ~ 20 pA peak-to-peak. These simulations suggest that it is possible to detect bubbles with radii > 80 nm under the conditions employed.

The resonance frequency ($f_0$) of a small bubble with a radius ($R_0$) of 100 nm assuming isothermal conditions, can be calculated using

\[ f_0 = \frac{3}{8} \frac{1}{2} \frac{\rho V}{\rho V} \frac{1}{2} \frac{R_0}{2} \]
and considering values of the surface tension in water\(^6\) \((\sigma, 0.072 \text{ N m}^{-1})\), density of the liquid \((\rho, 1000 \text{ kg m}^{-3})\); this yields a value of 85 MHz. The magnitude of the wall displacement amplitude \((R_{\infty})\) can then be calculated using,

\[
R_{e0} = \frac{P_a}{R_0 \rho \sqrt{\left(\omega_0^2 - \omega^2\right)^2 + (d_{tot} \omega^2)^2}^{1/2}}
\]

where \(P_a\) represents the acoustic pressure amplitude, \(\omega_0\) the bubble resonance frequency \((2\pi f_0)\), \(\omega\) the frequency of the sound considered \((2\pi f)\) and \(d_{tot}\) the dimensionless damping coefficient. The value of \(d_{tot}\) can be calculated following the method described by Eller\(^7\). Figure S7 shows how the value of \(d_{tot}\) and its various components change with bubble size. For nanobubbles, if the same assumptions apply, only viscous damping remains significant and even that is very small at \(R_0 = 100 \text{ nm}\).

![Graph showing the dimensionless damping coefficient, \(d_{tot}\), plotted as a function of bubble radius \((R_0)\) following the method described by Eller. The components for viscous, \(d_{visc}\), radiative, \(d_{rad}\) and thermal, \(d_{th}\) are included. Note this plot was calculated using the values reported for air bubbles in water reported by Eller in a 23 kHz sound field.](image)

Considering a 100 kPa 23 kHz sinusoidal excitation, the wall displacement amplitude \((R_{\infty})\) can be calculated to be \(\sim 3.4 \text{ nm}\) for a 100 nm bubble. This is mainly due to the large difference between the bubbles resonance frequency (85 MHz) and the excitation.
frequency (23 kHz). Note, it is unclear as to the physical forces that may exist at the nanobubble scale and how these impact on damping and resonance frequency. However, given the assumption made here, it appears that nanobubble oscillation under these conditions will be small. Modelling nanobubble translocation and using a 97 nm or 103 nm radius bubble yields a change in the translocation current of ~ 13 pA (peak-to-peak). Hence, given that this would imply that the zero-to-amplitude of the current oscillation would be ~7 pA, it is not surprising when the peak-to-peak noise is 20 pA that no nanobubble oscillation could be detected in the translocation transient. These considerations support the experimental data reported in the main manuscript.

Figure S8 shows the translocation of a polystyrene nanoparticle through a nanopore fabricated in the manner described in the main text. This translocation exhibits the asymmetric transient shape reported by others as expected.

![Graph](image)

Figure S8. Plot showing the translocation of a 600 nm polystyrene particle through an 800 nm conical nanopores. The solution contained 1 M KCl. A 1 V bias was placed across the pore between the internal and external Ag/AgCl electrodes. A pressure differential of 34 mbar was applied to drive pressure induced translocations.

Lastly, the effect of polarity on the translocations observed was investigated. Figure S9 shows results where the polarity applied to the pore was inverted. In this case transient nanobubbles were detected which also terminated after the ultrasonic irradiation of the system had been stopped.
Figure S9. Plots showing the ion current ($i$, ▬) for a 440 nm diameter pore and the acoustic pressure ($P$, ▬) as a function of time. The GNP was positioned ~1 mm laterally and level with the PLE (2 W$_{rms}$). The aerobic solution contained 10 mM KCl. A potential of -350 mV was applied across the pore. A pressure difference of 76 mBar was applied to draw liquid into the GNP. The solution temperature was ~23.5 °C.

References


(6) Kaye, G. W. C.; Laby, T. H. Tables of Physical and Chemical Constants and Some