Nanoscale Electrochemical charge transfer kinetics investigated by Electrochemical Scanning Microwave Microscopy.

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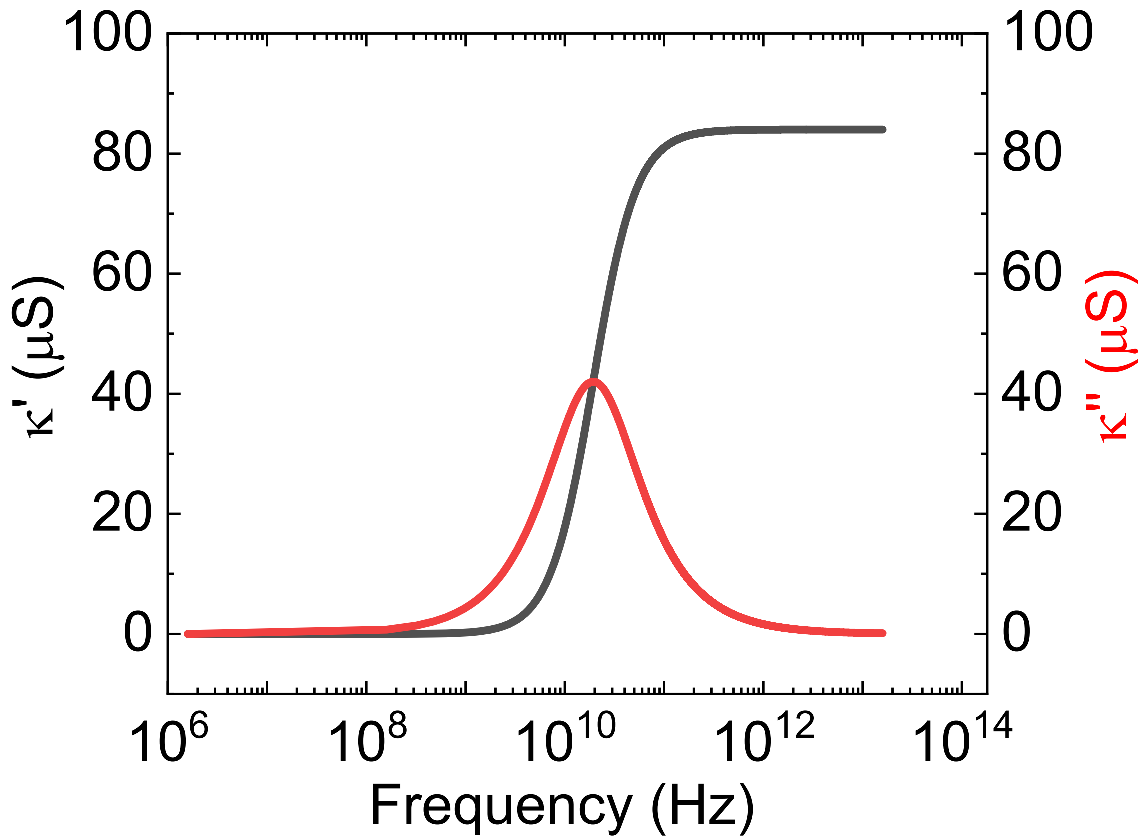

Figure S1 **The complex conductance against high frequency.** The black line is the real part of conductance κ' κ', the value of κ' κ' increases at $1/\tau \ll \omega$. The red line is the imaginary part of the complex conductance κ' κ', the value κ'' κ' is $\simeq 0$ at $1/\tau \ll \omega$

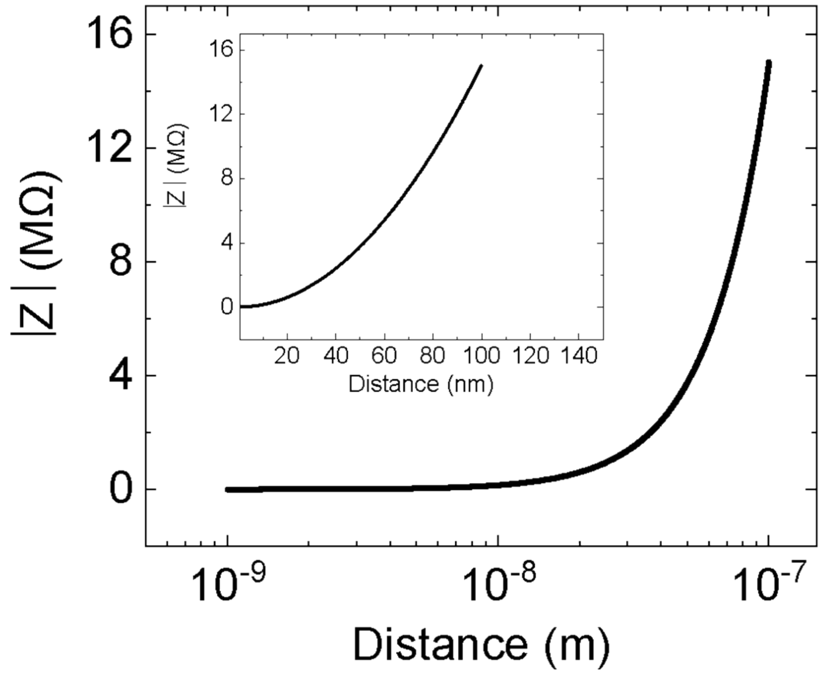

Figure S2 **solution impedance at different tip-sample distances.** The impedance rapidly increases at D at <100nm using equation 1.

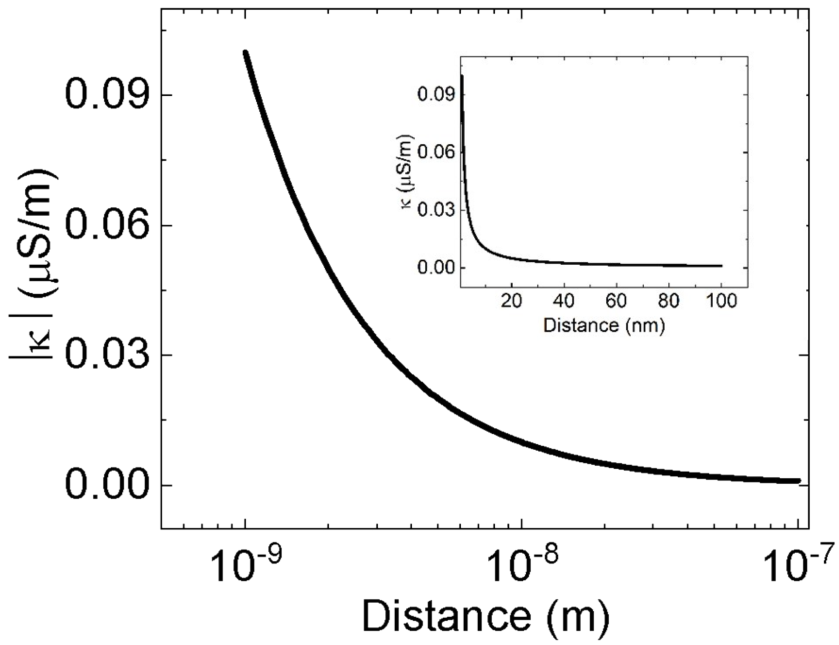

Figure S3 **shows how the conductance decays as the distance increases:** the conductance rapidly decreases at D at <100nm using equation 9

Supplementary Note 1. tip capacitance and radius

The measured current is proportional with area therefore:

$$\frac{I_G}{A_G} = \frac{I_L}{A_L}$$

Where I_G and A_G are the current of global CV and the whole area of the sample, I_L and A_L are the current of local CV and the area of the tip.

$$\frac{0.6 \times 10^{-6} A}{0 \cdot 25 cm^2} = \frac{16 \times 10^{-18} A}{A_L}$$

$$A_L = \frac{16 \times 10^{-18} A \times 0.25 cm^2}{0.6 \times 10^{-6} A} = 6.66 \times 10^{-12}\, cm^2 = 666 \pm 110\, nm^2$$

$$A = \pi r^2 = 666 \pm 110\, nm^2$$

$$r = 14 \pm 2\ nm$$

$$C_p = \frac{3\ (aA)}{666\ (nm^2) \times 0.01(\frac{V}{s})} = 45\ \mu F/cm^2$$

$$C = \frac{\varepsilon A}{d}$$

Where is d=0.1 nm, A=666 nm^2

$$\varepsilon = \frac{0.1 \times 10^{-9}\, m \ \times 45 \times 10^{-10} F}{666 x^{10^{-9}} m^2} = 0.675\ pF/m$$

Supplementary Note 2. Conductance change due to the increase of charge concentration

$Z_{tot} = Z_{sol} + Z_{SAM} = L/(\kappa^{'} + i\kappa^{''})A$

$Re(z) = d/(\kappa^{'} + i\,\kappa^{''})A$

$$Q_{ions} = Q_f(1 - \frac{Z_{SAM}}{Z_{tot}})$$

Where Z_{SAM} can be approximated to a parallel plate capacitor $C_{SAM} = \frac{\varepsilon_o \varepsilon_{r\,A}}{d}$

$$\kappa_\infty = \frac{c_{ions}}{c_{water}}\kappa_{\infty,water} = \frac{Q_{ions}}{F\,A\,L\,c_w}\kappa_{\infty,w} = \frac{\kappa_{\infty,w}}{F\,A\,L\,c_w}Q_{ions} = \frac{\kappa_{\infty,w}}{F\,A\,L\,c_w}Q_f(1 - \frac{Z_{SAM}}{Z_{tot}})$$

$$\kappa_\infty = \frac{Q_f \times \kappa_{\infty,w}}{F\,A\,L\,c_w}\left(\frac{Z_{tot} - Z_{SAM}}{Z_{tot}}\right) = \frac{Q_f \times \kappa_{\infty,w}}{F\,A\,L\,c_w}\left(\frac{Z_{sol}}{Z_{tot}}\right) = \frac{Q_f \times \kappa'_{\infty,w}}{F\,A\,L\,c_w}\left(\frac{Z_{sol}}{Z_{sol} + Z_{SAM}}\right)$$

$$z = \frac{1}{j\omega C} = \frac{1}{\frac{i\omega\varepsilon A}{d}} = \frac{d}{i\omega\varepsilon A}$$

$$\kappa_\infty = \frac{Q_f \times \kappa'_{\infty,w}}{F\,LA\,c_w}\left(\frac{(\frac{L}{i\omega A\varepsilon_w})}{(\frac{d}{i\omega A\varepsilon_w}) + (\frac{h}{i\omega A\varepsilon_{SAM}})}\right) = \frac{Q_f \times \kappa'_{\infty,w}}{FL\,A\,c_w}\left(\frac{(\frac{L}{\varepsilon_w})}{(\frac{d}{\varepsilon_w}) + (\frac{h}{\varepsilon_{SAM}})}\right)$$

$$\kappa_\infty = \frac{Q_f \times \kappa'_{\infty,w}}{F\,LA\,c_w}\left(\frac{(\frac{L}{\varepsilon^*_w})}{(\frac{\varepsilon^*_{SAM}d}{\varepsilon^*_{SAM}\varepsilon^*_w}) + (\frac{\varepsilon^*_w h}{\varepsilon^*_w\varepsilon^*_{SAM}})}\right) = \frac{Q_f \times \kappa'_{\infty,w}}{FL\,A\,c_w}\left(\frac{(\frac{L}{\varepsilon_w})}{(\frac{\varepsilon_{SAM}d + \varepsilon_w h}{\varepsilon_{SAM}\varepsilon_w})}\right)$$

$$\kappa_\infty = \frac{Q_f \times \kappa_{\infty,w}}{F\,A\,c_w}\left(\frac{\varepsilon_{SAM}}{\varepsilon_{SAM}L + \varepsilon_w h}\right)$$