

Observation of ionic Coulomb blockade in nanopores

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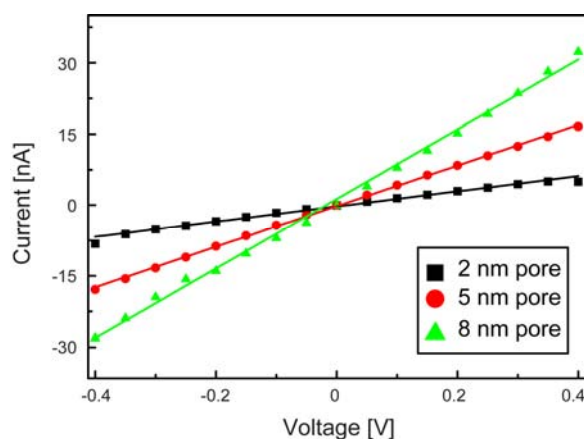
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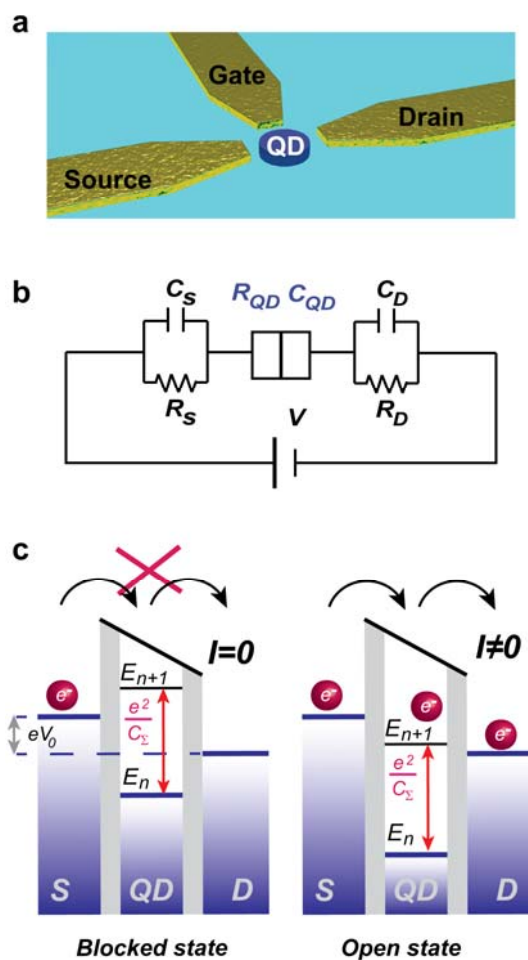
Membrane Material

We don't exploit any unique material properties of MoS₂ and same phenomenon of ionic Coulomb blockade can be also observed with any other 2-D material, hosting a sub-nm pore or 1-D nanotubes. In this study, MoS₂ membrane is used due to the simpler control in fabrication of individual sub-nm pores and better pore wetting compared to graphene. The criteria for the observation are mainly based on the device geometry with pore size range in 0.6 to 1 nm. The dielectric properties of the membrane materials are also relevant. We suggest the use of materials having dielectric constant one order of magnitude lower than water (80). Other information regarding nanopore fabrication process flow, characterization of the membrane by AFM and TEM, TEM based pore drilling, the fluidic cell design, custom-made Labview program for data acquisition, measurement setup and statistical analysis of the data can found in our previous work on MoS₂ nanopores^{1,2}.

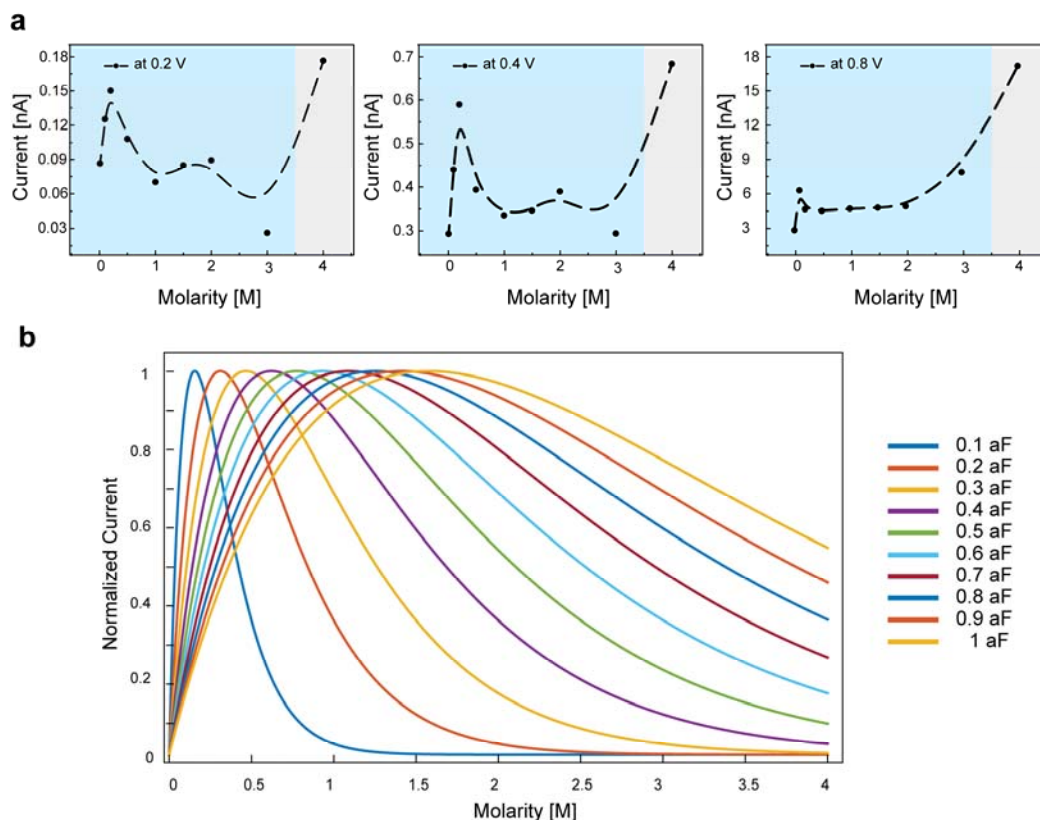
SI FIGURES



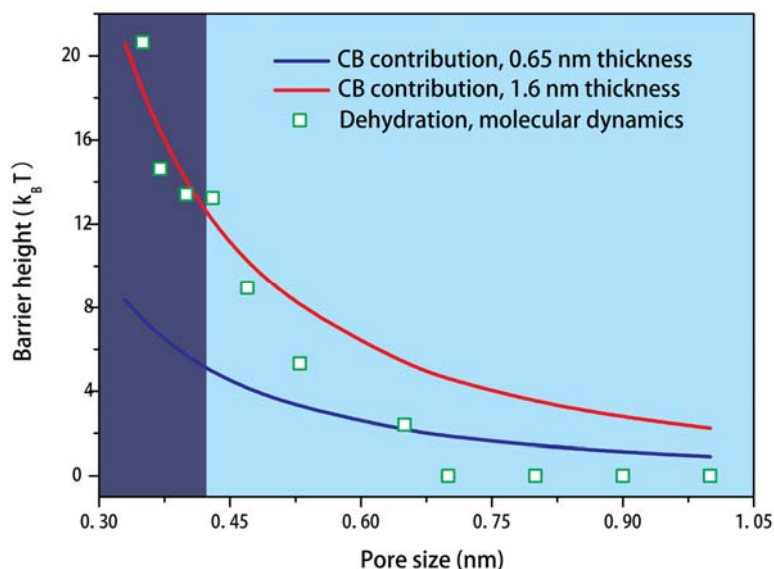
SI Fig 1. Examples of current-voltage I - V characteristics taken in 2 nm, 5 nm, and 8 nm MoS₂ nanopores using 1 M KCl, at pH 7. Ionic transport through a MoS₂ nanopore larger than 1 nm displays Ohmic behavior with linear I - V characteristics.



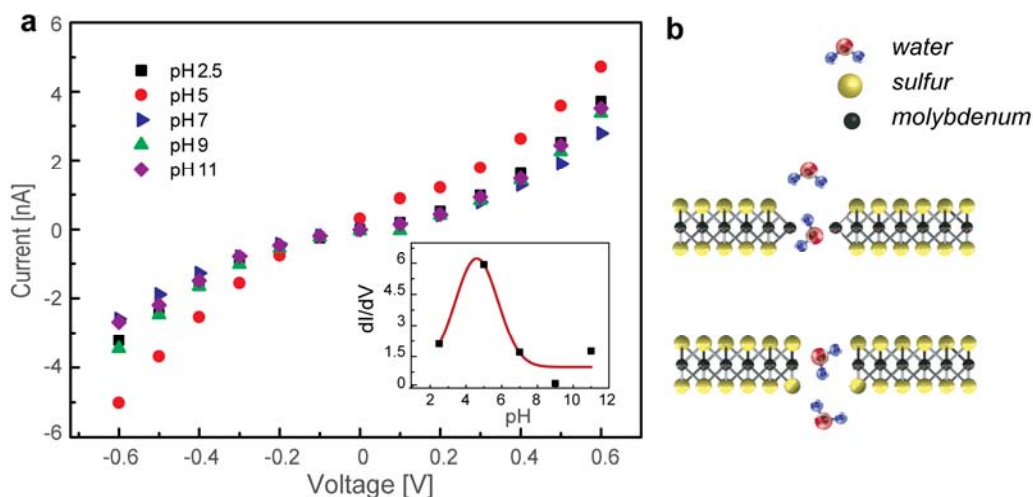
SI Fig 2. Proposed energy-level diagram of the single quantum dot. **a).** Illustration of the solid-state quantum dot device with a source, drain and gate electrode. **b).** Corresponding equivalent circuit for a system shown in (a). **c).** Energy level diagram for a for quantum dot system.



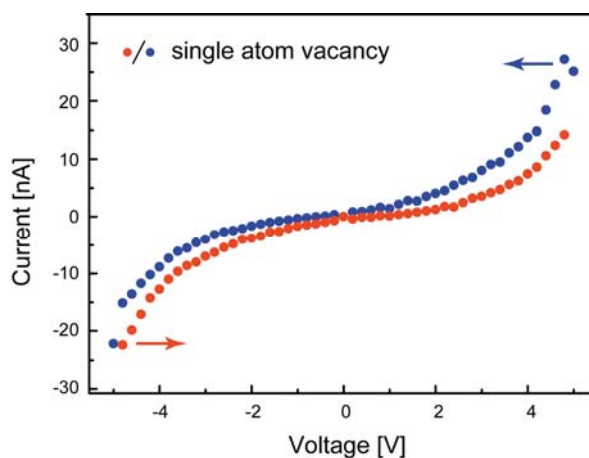
SI Fig 3. a). Current-molarity relation at 200 mV, 400 mV, 800 mV, respectively. Data taken from Fig 2. Gray region in the graphs indicates the ionic precipitation limit of KCl of about 3.5 M that can explain the large current obtained in 4 M KCl. On the other hand, a peak around 500 mM is found for all cases, which is another signature of ionic Coulomb blockade and can be fitted to plots in **b).** Theoretically predicted current-molarity relation at different pore capacitance. The equation is taken from the simulation work³, plotted with our device parameters, (pore diameter is set to 0.6 nm and we assumed simple cylindrical geometry of 3 atom thick pore, $L=0.65$ nm). The peak position highly depends on the pore capacitance. Peak position of 0.2 M corresponds to pore capacitance of 0.2 aF which is very close to the value estimated using the model presented in Fig.2 c.



SI Fig 4. The barrier heights for Coulomb blockade and dehydration. Coulomb energy is estimated using the equation 2 from the manuscript and dehydration data is taken from the molecular dynamics simulations^{4,5}. On the left side of the boundary diameter (0.4 nm), dehydration becomes relevant due to the breaking of strong second hydration shell. After the dash line (third hydration shell), contribution from dehydration is negligible.



SI Fig 5. Surface chemistry induced charge oscillation under various pH from another device. The pH peak is found around 5. The variations originate from surface chemistry combinations⁶⁻⁸ as shown **b**).



SI Fig 6. Current-voltage I - V measurements of an estimated 0.3 nm MoS₂ pore taken in 1 M KCl. A second scanning of I - V is taken to ensure the pore is not significantly enlarged by the application of high voltages.

Pore Geometry	Coulomb Energy Theoretical thickness 0.65 nm	Coulomb Energy Hydration thickness 1.6 nm	Dehydration barrier
0.3 nm diameter	10 k _B T	25 k _B T	70 k _B T (molecular dynamics ⁴)
0.6 nm diameter	3 k _B T	5 k _B T	2.4 k _B T (molecular dynamics ⁴)
0.8 nm diameter	1.4 k _B T	3.5 k _B T	Negligible (molecular dynamics ^{4,5})
1 nm diameter	0.9 k _B T	2 k _B T	Negligible (molecular dynamics ⁵)

Table 1. Estimated transport barrier

Ionic Coulomb blockade discussion

Here we summarize the following evidence in support of ionic Coulomb blockade model.

1. Low capacitance charging model

Geometry of MoS₂ nanopores (L=1.6 nm, d=0.6 nm) presented in this work is almost identical to the biological channel modeled by *Kaufman et al.*⁹ and the geometry-dependent self-capacitance of the channels is derived using a straightforward estimation for plate capacitor resulting in the small capacitance.

2. Valence-dependence

The Coulomb energy gap is not only a function of geometry but as well the valence and should results in the suppressed current for divalent ions, as measured in main **Fig. 3**.

3. Current molarity relation

The capacitance of the system can be extracted using current-molarity relation as suggested by the *Krems et al.*³. Although *Krems et al.* modeled a V shape nanopore, it is also noted in their work that the prediction should work for cylindrical small pores³. In fact, we obtained comparable values for capacitance using both approaches, when we applied straight-forward geometry based capacitance calculation we obtain capacitance of 1.2 aF, while capacitance obtained by fitting the current versus molarity data as proposed by *Krems et al.* yields 0.2 aF for experimental peak at 200 mM and 1 aF at 2 M. Such a tiny capacitance unambiguously leads to the direct observation of ionic Coulomb blockade at room temperature (**SI Fig. 3**). The second conductance “peak” around 2 M can be potentially due to different charge states (transitions from N+1 to N+2 charge states in the pore) but it may also refer to other possibilities since it occurs too close to the precipitation limit.

4. Conductance oscillations from surface charges

We used the pH to modulate the surface charges of the pore (MoS₂ is negatively charged and an increase of pH will add more negative charges to the pore) and a Coulomb oscillation has been found at certain voltages by the maximum conductance at the given pH values (**Fig. 4** and **SI Fig. 5**). The observed non-monotonic behavior is in good agreement with predictions by *Kaufman et al*⁹.

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