Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information to "Origin of Nonequilibrium $1/f$ Noise in Solid-State Nanopores"

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Theoretical model

When κ is dependent on the trap location in some situations, considering that the different trap location $\boldsymbol{r}$ corresponds to a different $\kappa(\boldsymbol{r})$, κ^2 in our formula (Eq. (6) in the manuscript) should be replace by an average quantity $\overline{\kappa^2}$ when calculating the $1/f$ noise, and $\overline{\kappa^2}$ can be expressed as

$$\overline{\kappa^2} = \iint_S \kappa^2(\boldsymbol{r})\rho_\kappa(\boldsymbol{r})\mathrm{dA}, \tag{1}$$

where A is the superficial area of the nanopore wall and the probability density function of the traps usually satisfies $\rho_\kappa = 1/A$ as we assume the traps distribute uniformly on the nanopore wall with the same probability of being occupied.

Calculations

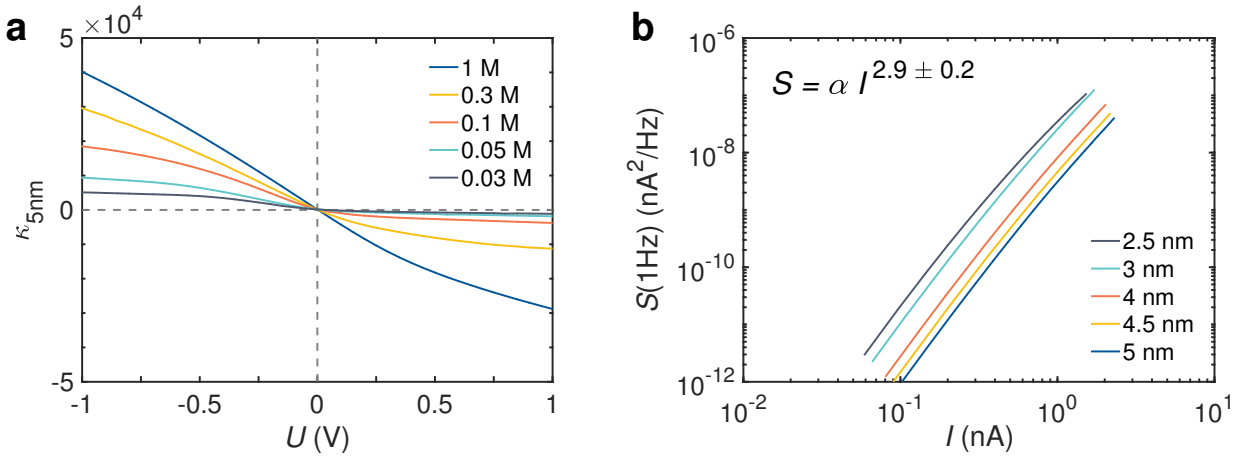

Fig. S 1: (a) Numerical calculations for $\kappa_{5\text{nm}}$ at different voltage U in a series of concentrations KCl for a conical nanopore with $r_\text{t} = 2.5$ nm, $r_\text{b} = 250$ nm, and $\sigma_0 = -0.08$ C/m^2. (b) Calculated $S(1\text{ Hz})$ at different current I in 0.1 M KCl for five conical nanopores with $r_\text{b} = 250$ nm, $\sigma_0 = -0.08$ C/m^2, and a series of r_t. These data are obtained at negative voltage, and results at positive voltage show the same rule (data not shown).

The numerical calculations of $\kappa_{5\text{nm}}$ for conical nanopores in various concentrations KCl with different r_t and σ_0 are respectively shown in Fig. S 1a, 2a, and 3a. The theoretical results of the normalized power spectrum of the ion current S/I^2 at f=1 Hz for conical nanopores with different r_t and σ_0 are respectively shown in Fig. S 2b and 3b with using a common Hooge parameter $\alpha_\text{H} = 1.1 \times 10^{-4}$ of solid-state nanopores.[1] The calculated power spectra of the ion current $S(1\text{ Hz})$ at different current I in 0.1M KCl for several conical nanopores with $r_\text{b} = 250$ nm, $\sigma_0 = -0.08$ C/m^2, and different r_t are shown in Fig. S 1b.

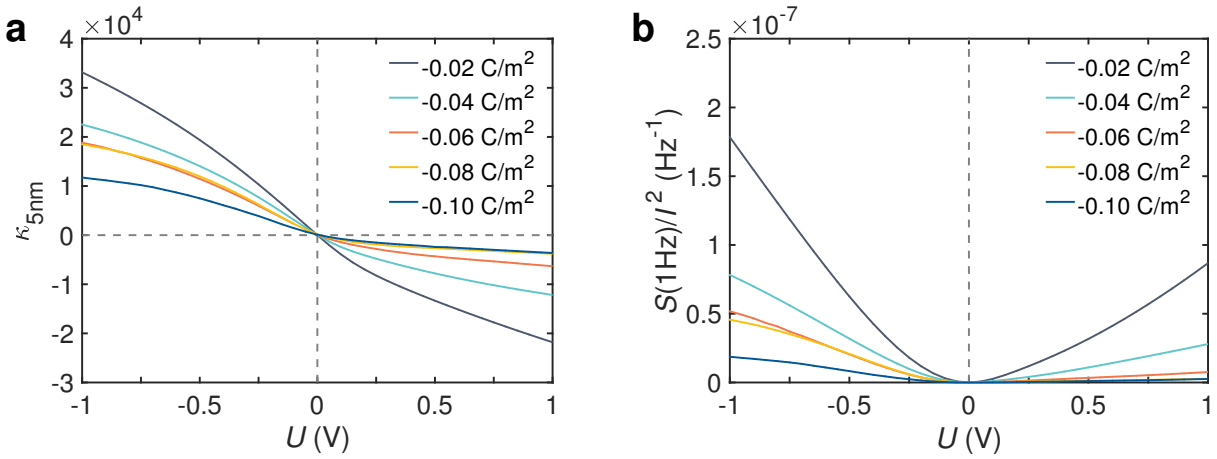

Fig. S 2: (a) Numerical calculations for $\kappa_{5\mathrm{nm}}$ at different voltage U in 0.1 M KCl for a conical nanopore with r_t = 2.5 nm and r_b = 250 nm, with different surface charge density σ_0. (b) Theoretical $S\,(1\ \mathrm{Hz})/\mathrm{I}^2$ for the same nanopore in (a).

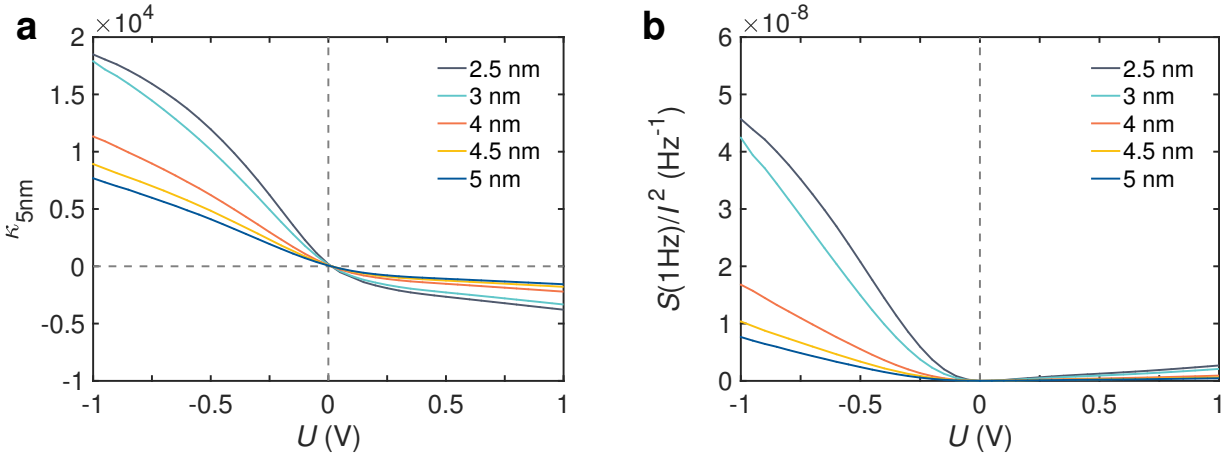

Fig. S 3: (a) Numerical calculations for $\kappa_{5\mathrm{nm}}$ at different voltage U in 0.1 M KCl for five conical nanopores with r_b = 250 nm, $\sigma_0 = -0.08\ \mathrm{C/m^2}$, and a series of r_t. (b) Theoretical $S\,(1\ \mathrm{Hz})/\mathrm{I}^2$ for the same nanopores in (a).

Experiments

The well-known asymmetric track-etching technique[2–8] was used to fabricate the single conical nanopore in experiments. A 12 μm thick polyethylene terephthalate (PET) film was first irradiated with a single Ar ion with energy of 11.4 MeV/nucleon at Heavy Ion Research Facility in Lanzhou (HIRFL), China. Then both sides of the film were irradiated under ultraviolet with intensity of $4.2 \times 10^3\ \mu\mathrm{W\ cm^{-2}}$ (MUA-165, MEJIRO GENOSSEN, Inc.) for one hour. After above two steps,

the PET membrane was fixed in the middle of a custom-designed system for subsequent track-etching, and the foil separated the two chambers where one contained the etchant of 2 M NaOH and the other contained the stop medium of 1 M HCOOH as well as 1 M KCl. The system was heating in water bath at the temperature of 60 °C. It is worth noting that considering the potentially slight changes of the properties of such a polymeric film, we modified the concentration of the etchant and the temperature, compared to our previous configurations of 9 M NaOH etchant at room temperature,[5] in order to effectively create a nanopore with large conical angle, where the noise would be more observable according to the studies on the influence of tip radius in the manuscript. During the whole etching procedure, we used a picoammeter (Keithley 6487, Keithley Instruments, Inc.) with platinum electrodes to monitor the ionic current across the foil, where a voltage of 1 V was applied at the side of the etchant. We could suddenly detected an increase of the current when the etchant penetrated through to the other side of the foil, which meant the birth of a conical nanopore with base entrance at the etchant side and tip entrance at the other. At the same time, the stop solution would immediately neutralize the etchant and the applied electric field could remove the hydroxide ions in the etchant from the tip entrance of the pore, which both could prevent further enlargement of the pore. Immediately after the detection of a formed pore, we removed the etchant from the chamber and replaced it with the stop medium. Finally, a single conical nanopore with a small tip entrance was fabricated, and it was washed with deionized water and kept for subsequent experiments.

Fig. S 4 shows the scanning electron microscope (SEM) image of the base entrance of conical nanopores fabricated using the asymmetric-etching technique described in the manuscript in the same condition with a slightly longer etching time. It is worth noting that the exhibited nanopores are not the one used in studying the $1/f$ noise in the experiments, because a single conical nanopore in a polyethylene terephthalate membrane with active area of ~ 1 cm^2 is hard to identify due to the random location of a single incident energetic ion. Therefore, multiple conical nanopores formed in the same condition are shown here. Besides, as the tip entrance of the conical nanopores is about several nanometers in radius, it is even much more difficult to be observed compared to the base

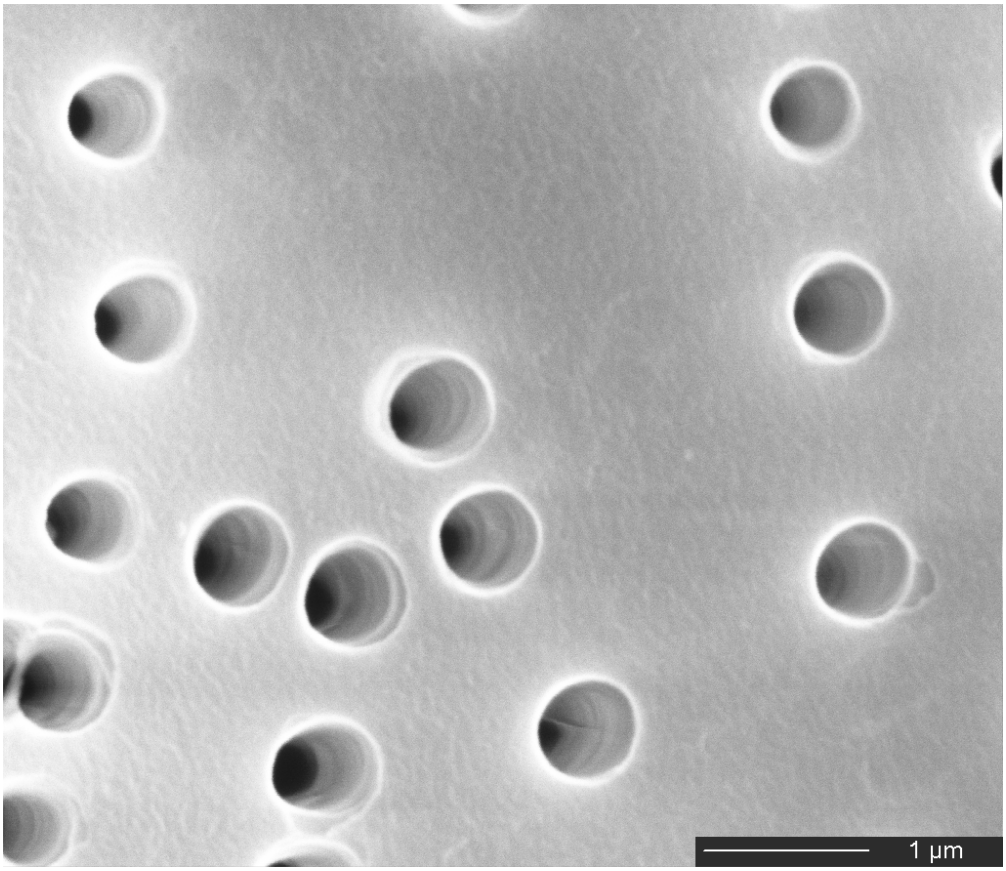

Fig. S 4: Scanning electron microscope (SEM) image of the base entrance of conical nanopores fabricated using the asymmetric-etching technique described in the manuscript.

entrance. Thus, the radius of the tip entrance is obtained by the electrical conductivity method as mentioned in the manuscript.

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