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## Origin of nonequilibrium $1/f$ noise in solid-state nanopores†

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Nanopore devices are applied in many fields such as molecular sensing and DNA sequencing, and the detection precision is primarily determined by  $1/f$  noise. The mechanism of  $1/f$  noise in nanopores is still not clearly understood, especially the nonequilibrium  $1/f$  noise in rectifying nanopores. Hereby, we propose that  $1/f$  noise in solid-state nanopores originates from the electrolyte ion trapping–detrapping process occurring on the inner surface of the nanopores, which can nonlinearly affect the ion number inside the rectifying nanopores due to the specific ion enrichment/depletion effect. Our model can not only quantitatively explain the nonlinear dependence of  $1/f$  noise on the applied voltage, *i.e.*, the nonequilibrium  $1/f$  noise, for current rectifying nanopores, but also provide a unified explanation on the influence of the electrolyte concentration, pH value, and geometry of the nanopores. From our model, we observe a new flattening phenomenon of  $1/f$  noise in conical nanopores, and this is further confirmed by our experimental results. Our research can be helpful in understanding and reducing  $1/f$  noise in other nanopore devices, especially where the enrichment or depletion of ions exists.

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### 1. Introduction

Solid-state nanopores have wide application in biophysics and nanotechnology for molecular sensing,<sup>1–3</sup> DNA sequencing,<sup>4–7</sup> biomolecule translocation detection,<sup>8–10</sup> DNA data storage,<sup>11</sup> and nanofluidic electronic devices.<sup>12–14</sup> These applications are based on an accurate analysis of the ion current through nanopores. Usually, nanopore devices are high-impedance systems, which require precise measurement of the ionic current, and therefore a high signal-to-noise ratio is of crucial importance for these devices. In particular, the noise level at a low frequency, which is known as  $1/f$  noise, governs the limit of detection for these devices,<sup>2–6,9,10</sup> so understanding the origin of  $1/f$  noise is beneficial for minimizing this noise and further improving the performance of solid-state nanopore devices.

$1/f$  noise is a general phenomenon in all nanofluidic systems and has been studied for decades.<sup>15–23</sup> Generally, the

Hooge formula can well describe this noise using a few parameters.<sup>4,15</sup> However, for current rectifying nanopores, it was recently found that  $1/f$  noise is nonequilibrium, *i.e.*, voltage-dependent, where the classical Hooge law is not valid anymore.<sup>16–18</sup> In order to figure out the origin of the  $1/f$  noise in nanopores, many models have been proposed, which attribute the  $1/f$  noise to bulk effects (like the fluctuation of solution temperature or viscosity,<sup>18</sup> changes in the pore geometry<sup>19,20</sup>), or interface effects (such as variations of the surface charge,<sup>21,22</sup> and nanobubble formation<sup>23</sup>). However, no agreement has yet been achieved. Although previous works have explained  $1/f$  noise in their special systems, none of them were able to describe the nonequilibrium  $1/f$  noise at a quantitative level. The reason is that these models were based on macroscopic effects and have not considered some special phenomena existing at the nanoscale, *e.g.*, the enrichment of ions in rectifying nanopores. Studying the mechanism of the nonequilibrium  $1/f$  noise is conducive to perfecting the application of rectifying nanopores, a highly valued type of nanopore, and also providing a framework to study and control  $1/f$  noise in other confined areas.

In this paper, we develop a new model to explain  $1/f$  noise in solid-state nanopores. The trapping–detrapping process of the electrolyte ions on the inner surface of the nanopore is proposed to be the major source of  $1/f$  noise. Our model can quantitatively describe the  $1/f$  noise in conical nanopores and also successfully predict the effects of electrolyte concentration, pH value, and nanopore geometry. The theoretical

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results of the noise indeed present nonequilibrium behaviors, which is consistent with the experimental results. With this model, we also find and explain a novel phenomenon of  $1/f$  noise in a conical nanopore, confirmed by our experiment. Our work provides clues to study  $1/f$  noise and improve the properties of related nanopore devices such as those used for DNA sequencing.

## 2. Model

Generally, the surface of a solid-state nanopore is charged,<sup>16–26</sup> and each charged site can serve as a trap to bind or release an electrolyte ion as schematically illustrated in Fig. 1. This situation can be viewed as two states for an ion: a “free” state with an energy of  $E_a$  where the ion stays inside the nanopore and a “bound” state with an energy of  $E_b$  where the ion is localized in a potential well on the nanopore wall with the activation energy  $E = E_a - E_b$  for the ion to detrapp. Therefore, the transition between the two states is a trapping–detrapping process, which can induce fluctuation of the total ion number inside the nanopore, thereby causing electrical noise in the measured ion current.

Each ion trap on the wall with an activation energy  $E$  corresponds to trapping–detrapping processes of the characteristic time  $\tau$  (Fig. 1), which can be described as<sup>27</sup>

$$\tau = \tau_0 e^{\frac{E}{k_B T}}, \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and the prefactor  $\tau_0$  is on the order of  $10^{-4}$  s.<sup>27</sup> Considering a situation where an ion gets trapped at a charged site on the nanopore wall, the electrostatic energy can be estimated to be on the order of 0.06–0.26 eV by the coulombic law, given that the ion–ion distance is about 0.7–3 Å in this case, so the energy  $E$  should be of the same order of magnitude as well, which varies for different traps. Therefore, the frequency  $f$  of the trapping–detrapping process is 0.1–160 Hz by eqn (1), and it falls in the range of low-frequency  $1/f$  noise.

The trapping and detrapping of ions cause fluctuation of the unfilled trap number  $n_t$ , so we take the power spectrum of

the trap number  $S_n$  into account. As each of these events is independent,  $S_n$  can be obtained by McWhorter theory:<sup>28</sup>

$$S_n(f) = \frac{\overline{\Delta n_t^2} k_B T}{f \Delta E}, \quad (2)$$

where  $\overline{\Delta n_t^2}$  is the variance of the fluctuation of the trap number and  $\Delta E$  is the range of  $E$ , which is around 0.2 eV, as mentioned above. When a single ion detraps from the surface, the empty trap number increases by one, which leads to a change in the total ion number inside the nanopore. A parameter  $\kappa$  is introduced here to describe such a difference in the ion number before and after a detrapping event. Thus, the fluctuation of the total ion number  $\delta N$  can be described by the fluctuation of the trap number  $\delta n_t$ :

$$\delta N = \kappa \delta n_t. \quad (3)$$

Based on eqn (3), the power spectrum of the ion number in the nanopore  $S_N$  satisfies

$$S_N = \kappa^2 S_n. \quad (4)$$

$S_N$  has an explicit relationship with the ion current noise, indicated by the power spectrum of the ion current  $S$ , which follows:<sup>29</sup>

$$\frac{S}{I^2} = \frac{S_N}{N^2}, \quad (5)$$

where  $I$  is the ion current and  $N$  is the ion number. Combining eqn (2), (4) and (5) and comparing with the Hooge formula,<sup>30</sup> we obtain

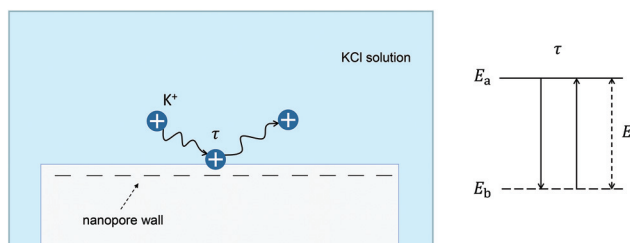
$$\frac{S}{I^2} = \kappa^2 \frac{\alpha_H}{fN}, \quad (6)$$

where  $\alpha_H$  is the Hooge parameter and  $\alpha_H = \overline{\Delta n_t^2} k_B T / N \Delta E$ . Eqn (6) shows the low-frequency  $1/f$  noise of the ion current as a result of the trapping–detrapping process.

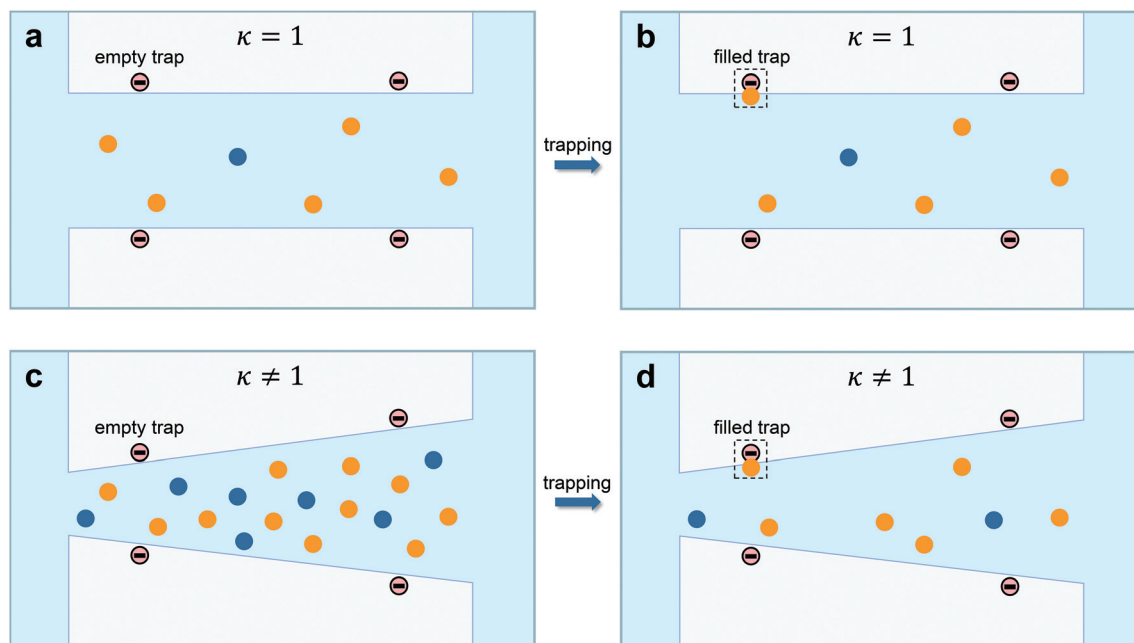
The factor  $\kappa$  can quantitatively describe the  $1/f$  noise in a nanopore. In the situation where  $\kappa = 1$ , an ion trapping process makes the number of the ions inside the nanopore decrease by one as schematically illustrated in Fig. 2a and b, and eqn (6) degenerates to the classical Hooge formula. When  $\kappa \neq 1$ , the ion number can change to much more than one even if only one trapping event occurs, as shown in Fig. 2c and d. As in such cases,  $1/f$  noise can only be described by our formula.

## 3. Results

The  $1/f$  noise in conical nanopores is investigated to test our model, because there has been no satisfactory explanation for the noise since it was found to be nonequilibrium in conical nanopores, the most important rectifying nanopores.<sup>16–18</sup> The value of  $\kappa$  is calculated from the change in the ion concentration upon detrapping of an ion from the nanopore wall. Given that  $c_i$  and  $c'_i$  are respectively the ion concentration dis-



**Fig. 1** Schematic illustration of the trapping–detrapping process of a single ion (e.g.,  $K^+$ ) on a negatively charged nanopore wall in potassium chloride solution.  $\tau$  is the characteristic time of the whole trapping–detrapping process.  $E_a$  and  $E_b$  are respectively the free and bound state energy of  $K^+$ , and the activation energy  $E = E_a - E_b$ .



**Fig. 2** Schematic illustration of the influence of a single trapping process of an ion on the total ion number inside a nanopore. The cations (yellow ball) and anions (blue ball) stay in the cylindrical or conical nanopore where  $\kappa = 1$  (a) and not equal to 1 (c) before and after (b) and (d) the trapping process, respectively.

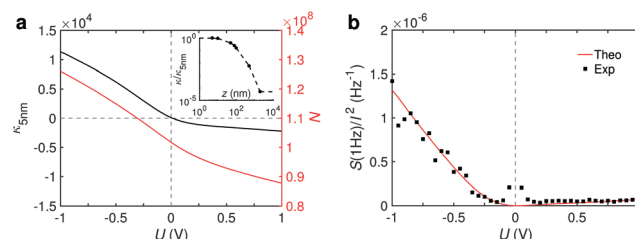
tributions inside the nanopore before and after a detrapping event,  $\kappa$  satisfies

$$\kappa = N_A \iiint_{V_p} (c'_i - c_i) dV_p, \quad (7)$$

where  $N_A$  and  $V_p$  are the Avogadro constant and the inner volume of the nanopore, respectively. For an arbitrarily shaped conical nanopore,  $c_i$  and  $c'_i$  can be numerically solved by Poisson–Nernst–Planck equations using COMSOL Multiphysics 5.3a (COMSOL, Inc.), and the details can be found in our previous work.<sup>31</sup>

As an example, we calculate  $\kappa$  for a single conical nanopore with a length of 12  $\mu\text{m}$ , radii of 4 nm ( $r_t$ ) at the tip and 250 nm ( $r_b$ ) at the base, and surface charge density  $\sigma_0 = -0.08 \text{ C m}^{-2}$ , and the electrolyte is an aqueous solution of potassium chloride at a temperature of 298 K. Fig. 3a shows the variation of  $\kappa$  with respect to the applied voltage  $U$ , provided that the trap locates at 5 nm from the tip entrance. The results clearly show that  $\kappa$  is far more than one for a conical nanopore and it increases with the voltage  $U$  in both polarities. It should be noted that the value of  $\kappa$  depends on the location of the traps (see the inset in Fig. 3a), and the  $\kappa$  value decreases with an increase in the distance of the traps from the nanopore tip opening.

We reckon that the voltage dependent feature of  $\kappa$  results from the enrichment/depletion of ions inside the conical nanopore.<sup>16–18</sup> The value of  $\kappa$  is directly determined by the degree of the enrichment or depletion effects, which can be reflected by the ion number inside the nanopore. As shown in Fig. 3a, when the voltage is negatively increased, the ion



**Fig. 3** (a) Black line: numerical calculations for  $\kappa_{5\text{nm}}$  at different voltages  $U$  in 0.1 M KCl, using a conical nanopore with  $r_t = 4 \text{ nm}$ ,  $r_b = 250 \text{ nm}$ , and  $\sigma_0 = -0.08 \text{ C m}^{-2}$ . Red line: the ion number  $N$  before the detrapping process when calculating  $\kappa_{5\text{nm}}$ . Inset:  $\kappa$  at different trap locations at  $-1 \text{ V}$  in 1 M KCl.  $z$  indicates the distance between the trap and the tip entrance of the nanopore along the central symmetrical axis  $z$ . Dots: data normalized by  $\kappa_{5\text{nm}}$ . Dashed line: the appropriate normalized weight  $f(z)$  of different locations by linear interpolation. (b) Theoretical  $S(1 \text{ Hz})/I^2$  in 0.1 M KCl calculated for the conical nanopore in (a), compared to the experimental data in 0.1 M KCl at a pH value of 8 for a polyethylene terephthalate (PET) conical nanopore with  $r_t = 4 \text{ nm}$ , and  $r_b = 200 \text{ nm}$ .<sup>16</sup>

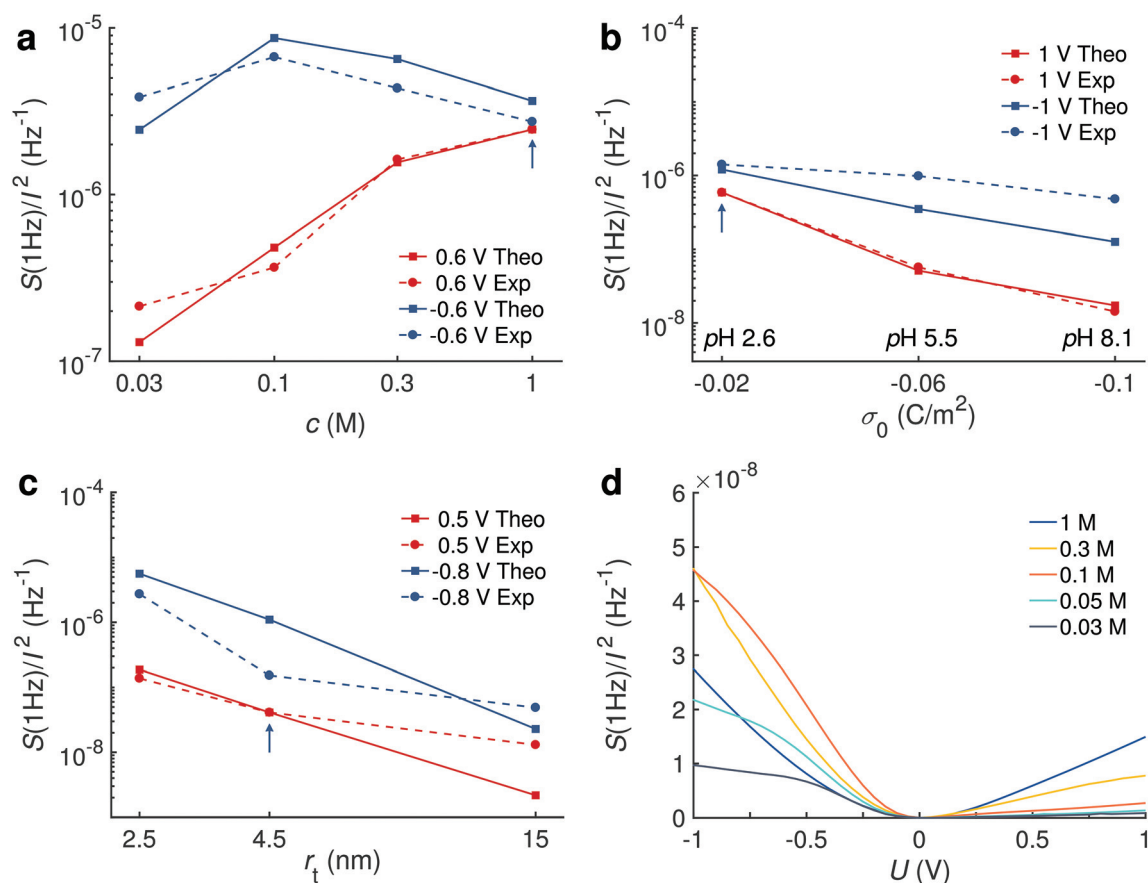
number appreciably increases, indicating that the ions are enriched inside the nanopore, thereby resulting in a significant increase in the  $\kappa$  value. At a positive voltage, although the depletion of ions intensifies with the voltage, the ion number is smaller than that at a negative bias voltage and supposed to show a slighter change caused by trapping–detrapping events, causing the  $\kappa$  value to increase a little with the voltage.

The normalized power spectrum of the ion current  $S/I^2$  can be obtained by eqn (6), and the trap position dependence of  $\kappa$  has been included in the calculations (for details see the ESI

section ‘Theoretical model’†). Fig. 3b shows the calculated  $S/I^2$  at  $f = 1$  Hz for the conical nanopore in 0.1 M KCl with the opening radii of 4 and 250 nm, and the corresponding experimental data are also presented for comparison. The theoretical results are normalized by the experimental value at  $-0.8$  V to account for the Hooge parameter of the actual nanopore. Clearly, the theoretical results well match with the experimental ones.  $1/f$  noise is much smaller at the positive voltage side than that at the negative voltage side with a negligible voltage dependence, which can be explained by the tendency of  $\kappa$ , as shown in Fig. 3a. The small value of  $\kappa$  indicates that the fluctuation in the ion number caused by the trapping-detrapping processes is negligible, which causes the small  $1/f$  noise. In contrast, the noise is large and increases rapidly with the applied negative voltage  $U$ , resulting from factor  $\kappa$  increasing with voltage. The specific correlation between  $\kappa$  and the noise is complicated as described by eqn (6). In summary, the nonequilibrium  $1/f$  noise can be described by the crucial factor  $\kappa$ , which is determined by the voltage-dependent ion

enrichment/depletion effect. Fig. 2c and d schematically show that the ion enrichment effect in a conical nanopore can result in a large  $\kappa$  value.

The above model can also be used to explain the dependence of  $1/f$  noise on other important factors, such as the electrolyte concentration  $c$ , pH value, and the radius of the nanopore tip entrance  $r_t$ .<sup>16–18</sup> Representative calculation results are shown in Fig. 4, and more detailed results are provided in Fig. S1, S2, and S3.† As shown in Fig. 4a–c, the calculated  $S(1\text{ Hz})/I^2$  at given voltages are compared with the corresponding experimental data, and their good agreement clearly indicates the validity of our model. For concentration dependence, when the voltage is negative the noise level first increases with the concentration and then decreases, whereas, when the voltage is positive, the noise increases monotonously with the concentration. As for the dependences on the pH value and radius  $r_t$ ,  $1/f$  noise increases at both positive and negative voltages when the two values are lowered. The results are in good agreement with the fact that the ion enrichment and depletion are also



**Fig. 4** (a)–(c) Theoretical and experimental  $S(1\text{ Hz})/I^2$  at certain voltages in different KCl concentrations (a), pH values (b), and  $r_t$  (c). The controlled parameters of the conical nanopore in the calculations are  $r_t = 2.5$  nm,  $r_b = 250$  nm,  $\sigma_0 = -0.08\text{ C m}^{-2}$ , and 0.1 M KCl. The experimental data are respectively for a PET nanopore with  $r_t = 3.5$  nm at pH 8 KCl<sup>18</sup> (a), a polyimide nanopore with  $r_t = 1$  nm and  $r_b = 500$  nm in 0.1 M KCl<sup>16</sup> (b), and PET nanopores at 0.1 M pH 8 KCl<sup>17</sup> (c). There is a positive correlation between the pH value and the absolute value of  $\sigma_0$ , but no specific relationship. So the pH values are roughly characterized by  $\sigma_0$ . All the theoretical results are normalized by the experimental values respectively in (a), (b) and (c), which are marked by arrows. (d) Theoretical  $S(1\text{ Hz})/I^2$  at different voltages  $U$  in a series of concentrations of KCl for a conical nanopore with  $r_t = 2.5$  nm,  $r_b = 250$  nm, and  $\sigma_0 = -0.08\text{ C m}^{-2}$ , using a common Hooge parameter  $\alpha_H = 1.1 \times 10^{-4}$  in nanopores.<sup>15</sup>

affected by  $c$ , pH values, and  $r_t$ .<sup>16–18</sup> Since factor  $\kappa$  depends on the degree of the enrichment/depletion of ions, parameters affecting this degree can change the  $1/f$  noise as a consequence. Notably, the above results give information on which factors should be most carefully adjusted in order to suppress the  $1/f$  noise in nanopores.

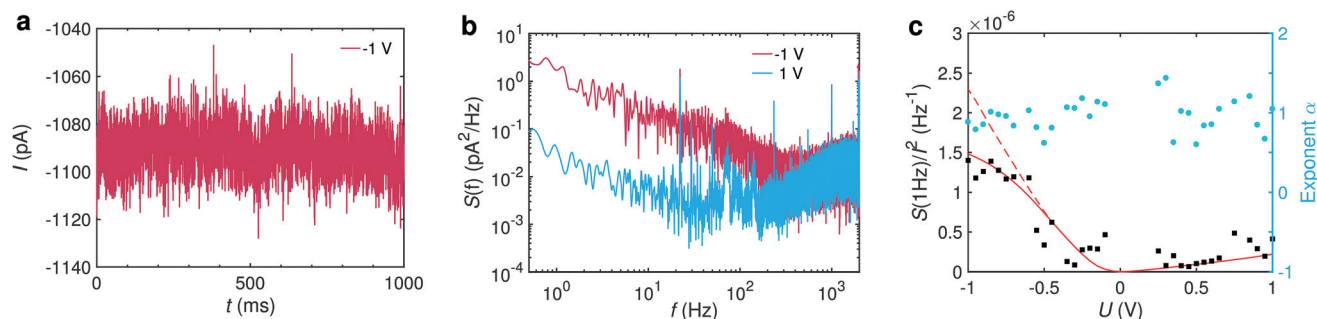
It is worth noting that the  $1/f$  noise in conical nanopores often increases steeply in the negative voltage range, as shown in Fig. 3b and other previous reports.<sup>16–18</sup> We find that under some special conditions the noise level could flatten out at a high negative voltage as shown in Fig. 4d. The flattening of the  $1/f$  noise tends to appear in a diluted solution (see Fig. 4d) with a high pH value and a small  $r_t$  (shown in Fig. S2b and S3b†). At a high negative voltage, the electric field in the nanopore is very strong so that almost all the ions near the tip opening of the nanopore are driven into the nanopore. Because the ion number near the tip is not very large,<sup>32</sup> further increasing the voltage has only limited effect in promoting the ion enrichment, so the increase in the rate of  $\kappa$  becomes lowered (as shown in Fig. S1a, S2a and S3a†) and the  $1/f$  noise level flattens out.

We conducted some experiments to verify this finding. The single conical nanopore used in experiments was fabricated by the well-known asymmetric track-etching technique.<sup>16–18,31–34</sup> Briefly, a 12  $\mu\text{m}$  thick polyethylene terephthalate film was first irradiated with a single energetic ion (Ar) with an energy of 11.4 MeV per nucleon, and then it was asymmetrically etched with 2 M NaOH as the etchant and the stop medium of 1 M HCOOH as well as 1 M KCl at 60 °C. Further details of the experimental method can be seen in the ESI.† It is worth noting that this fabrication procedure was known to lead to the formation of the so-called conically shaped pores, which may be actually trumpet-shaped or other shapes rather than being ideally conical.<sup>33,34</sup> Nevertheless, it is quite complicated to accurately obtain the actual shape of the formed pores, and other approximations of the pore geometry might also have some deviations. Therefore, we treated our pore as an ideally

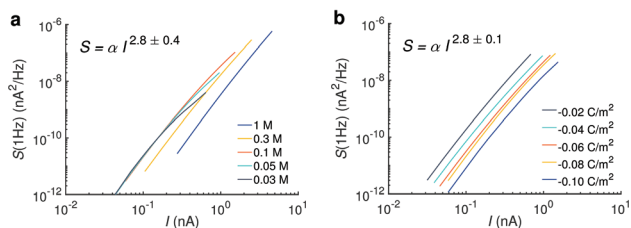
conical one in the same way as reported in ref. 16–18 and estimated that the nanopore had a base entrance radius of 250 nm and a tip entrance radius of 2 nm as determined by the electrical conductivity method described in our previous work.<sup>31</sup> Fig. S4† shows the scanning electron microscopy image of the base entrance of conical nanopores formed under the same conditions as an example. This conical approximation is only used to describe the created pore, which has no influence on subsequent experimental results.

When studying the noise in the conical nanopore, a patch clamp (MultiClamp 700B, Axon Digidata 1550B, Molecular Devices, Inc.) was used to record the ion current series. Ag/AgCl electrodes were used, and the electrode on the tip entrance was referenced to zero voltage. The sampling frequency was 10 kHz, and a low-pass Bessel filter of 1.4 kHz was used to filter the signals. Fifty second long ion current time series were studied in the voltage range between  $-1000$  mV and  $+1000$  mV with a 50 mV step. A frequency regime between 0.5 Hz and 1 kHz was chosen when calculating the power spectra to analyze the data.

Fig. 5 shows the experimental results of the flattening phenomenon. The examples of the ion current in the time series are presented in Fig. 5a, showing the fluctuation of the current. Fig. 5b shows two representative experimental curves of the power spectra of the ion current, and the noise in the low frequency region is indeed  $1/f$  noise. Fig. 5c shows a comparison of the experimental data of  $S(1\text{ Hz})/I^2$  with the calculation results. It is quite obvious that in the high negative voltage range, the experimental results of noise (black dots) are in good agreement with the calculation results from our model (solid line) but considerably smaller than that predicted from the low-voltage results (dashed line). The flattening phenomenon has been successfully observed in the experiments. These results indicate that  $1/f$  noise would be less voltage dependent in some situations, which can be useful for controlling the noise.



**Fig. 5** (a) Examples of ion current signals in time recorded in experiments for a PET conical nanopore with opening radii of 2 and 250 nm. The data were recorded in 0.1 M KCl, pH 7.23, at 23.8 °C. (b) Power spectra of ion current recorded for the nanopore (a) at two voltages. (c) Black dots: experimental  $S(1\text{ Hz})/I^2$  for the nanopore in (a). Solid line: theoretical  $S(1\text{ Hz})/I^2$  in 0.1 M KCl for a conical nanopore with  $r_t = 2$  nm,  $r_b = 250$  nm, and  $\sigma_0 = -0.08\text{ C m}^{-2}$ , normalized by the experimental value at  $-0.45$  V. Dashed line: prediction of  $S(1\text{ Hz})/I^2$  at a high negative voltage from the low-voltage results. Blue dots: exponent  $\alpha$  of a fitting power law relationship  $1/f^\alpha$  in appropriate frequency ranges for the conical nanopore in experiments when every power spectrum was analyzed.<sup>16,17</sup> In some cases, the power spectra are obviously not  $1/f$  noise results ( $\alpha > 2$  or  $< 1$ ), and these data are excluded.



**Fig. 6** (a) Calculated  $S(1\text{ Hz})$  at different currents  $I$  in a series of concentrations of KCl for the conical nanopore with  $r_t = 2.5\text{ nm}$ ,  $r_b = 250\text{ nm}$ , and  $\sigma_0 = -0.08\text{ C m}^{-2}$ . (b) Calculated  $S(1\text{ Hz})$  at different currents  $I$  in 0.1 M KCl for the conical nanopore with  $r_t = 2.5\text{ nm}$ ,  $r_b = 250\text{ nm}$ , and different  $\sigma_0$  values.

The above results indicate that the  $1/f$  noise in conical nanopores relates to many other factors besides applied voltage. It is surprising to note that  $1/f$  noise follows the relation proportional to  $I^{0.8}$  such that

$$S(1\text{ Hz})/I^2 = \alpha I^{0.8}, \quad (8)$$

for a fairly large range of  $c$ , pH value, and  $r_t$ , where  $\alpha$  is a pre-factor (see Fig. 6 and Fig. S1a†). Although the exact reason remains elusive, this relationship implies that the  $1/f$  noise in conical nanopores is current-dependent rather than voltage-dependent. Therefore, an effective way to lower the normalized power spectrum of the ion current is to operate the nanopore devices at a small ion current.

## 4. Conclusions

We propose a model to explain the origin of  $1/f$  noise in solid-state nanopores, based on the trapping–detrapping process of electrolyte ions on the inner surface of the nanopore. The behavior of  $1/f$  noise in nanopores is determined by the crucial factor  $\kappa$ . In some nanopores such as the cylindrical ones,  $\kappa = 1$ , so  $1/f$  noise can be described by the classical Hooge formula. When the ion enrichment/depletion effect occurs, which exists extensively in various nanopore devices,  $\kappa$  might be neither one nor a constant, and therefore,  $1/f$  noise possesses nonequilibrium features. Our model would also be valid in other nanopore devices with different geometry or distribution of surface charge density, *e.g.*, triangular nanopores and bipolar nanochannels,<sup>26,35</sup> as long as there is interaction between the ions and the pore walls. In order to reduce  $1/f$  noise in nanopores, lowering the  $\kappa$  value is an effective method like doing some modifications to the nanopore walls to decrease the number of ion traps.

## Conflicts of interest

There are no conflicts to declare.

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