Supplementary Information

On Stochastic Reduction in Laser-Assisted Dielectric Breakdown for Programmable Nanopore Fabrication

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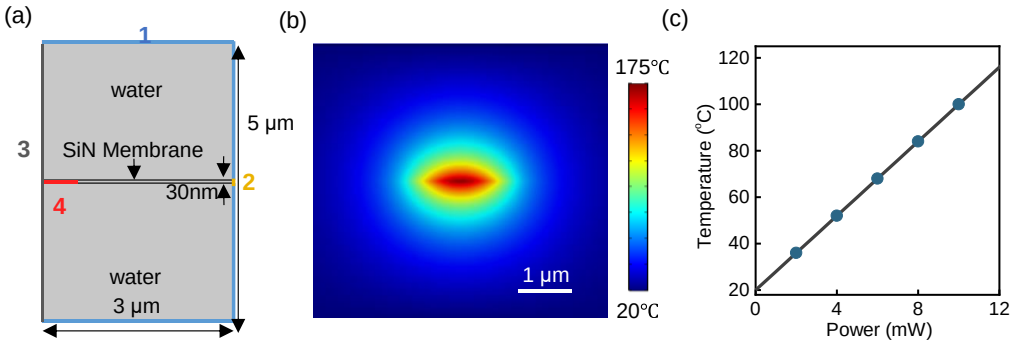
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This PDF file includes:

- Figures S1 to S8
- Tables S1 to S4
- Supplementary References

Supporting Figures



(d)

Boundary	Condition
1	Convection heat flux $q_c = h(T_0-T)$, $T_0 = 293$
2	Insulator
3	Axial symmetry
4	Heat source= Q

(e)

Parameters	Meaning	Value	Unit
$n1$	SiN_x refractive index	2.25	
$n2$	Water refractive index	1.3	
R	Reflection	$(n_1-n_2)^2/(n_1+n_2)^2$	
q	Quantum yield	0.07	
α	SiN_x absorption	10^4	1/cm
w	Laser spot radius	1×10^{-6}	m
P	Laser power	Variable	mW
I	Laser intensity	$2P/(\pi w2)$	W/m^2
Q	Heat source	$\alpha I(1-q)(1-R)$	W/m^3
h	Water heat transfer coefficient	50	W/m^3K

Figure S1. Finite-element simulation to study the photothermal heating of the solution. Heat transfer model was implemented by applying the first law of thermodynamics. (a) The physical domain used for simulation. A 30-nm-thick SiN_x membrane was placed in the middle of the simulation domain and surrounded by water. At the bottom of the SiN_x membrane, a heat source (Q) with Gaussian distribution of intensity was applied on an area with a radius of 1 μm to simulate the focused laser radiation. (b) Steady-state temperature profile under a 20 mW laser. The peak temperature is located in the center of the spot and quickly decreases to room temperature. The maximum temperature caused by the 20 mW laser was 175 °C, which is far below the SiN_x decomposition temperature. (c) Peak temperature as a function of laser power. The temperature increases linearly with laser power. The slope of the line is the photothermal coefficient (8.06 K/mW). (d) Boundary conditions used in simulation. (e) Parameters used in simulation.

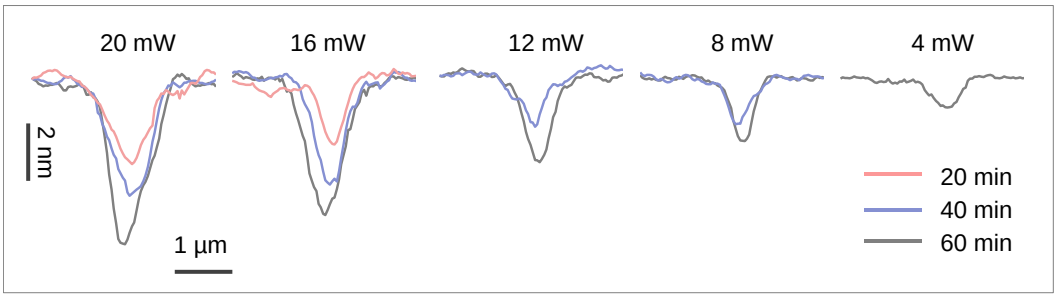


Figure S2. AFM-obtained etching profiles in **Figure 2d**.

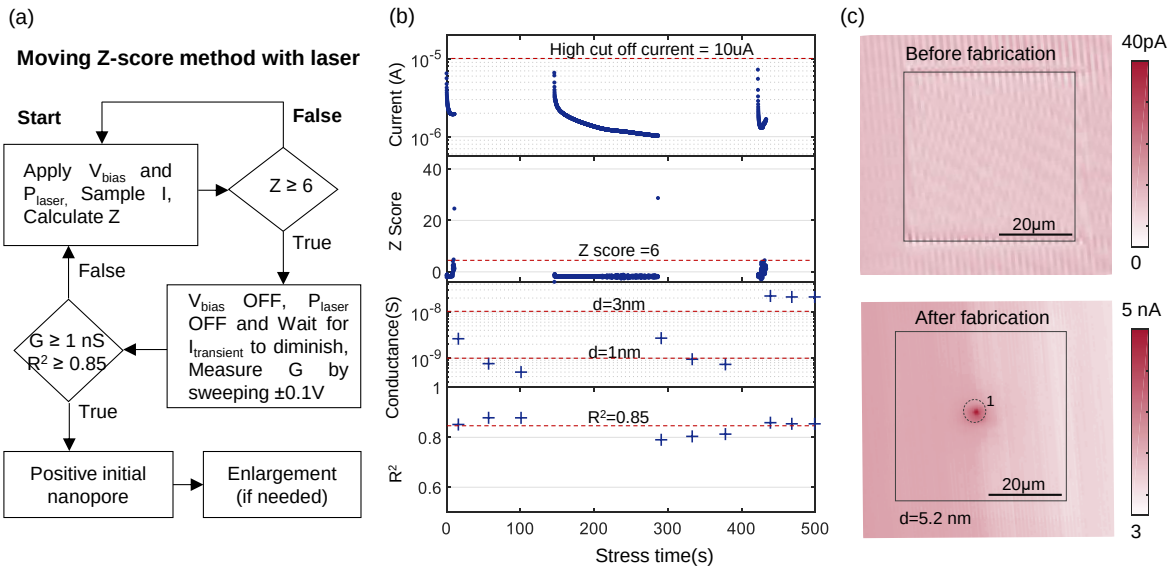


Figure S3. (a) Flowchart of the automated procedure for laser-assisted breakdown nanopore fabrication. The moving Z-Score is an online adaptive learning algorithm for detecting the abnormal points in a time-trace. It measures the number of standard deviations each new observation is away from the mean over a pre-defined time window length of w, $Z_k = \frac{I_k - mean(I_{k-1}: I_{k-w})}{std(I_{k-1}: I_{k-w})}$. The detailed description of the moving Z-score method can be found in our previous work [1]. (b) A representative nanopore fabrication process at 0.8 V/nm and 20 mW. The nanopore diameter estimated by the conductance measurement was about 5.2 nm. (c) Scanned ionic current mapping before (top) and after (bottom) the nanopore fabrication. Ionic current mapping experiments were performed at 4 mW laser power and 100 mV voltage with 10 µm/s scanning speed.

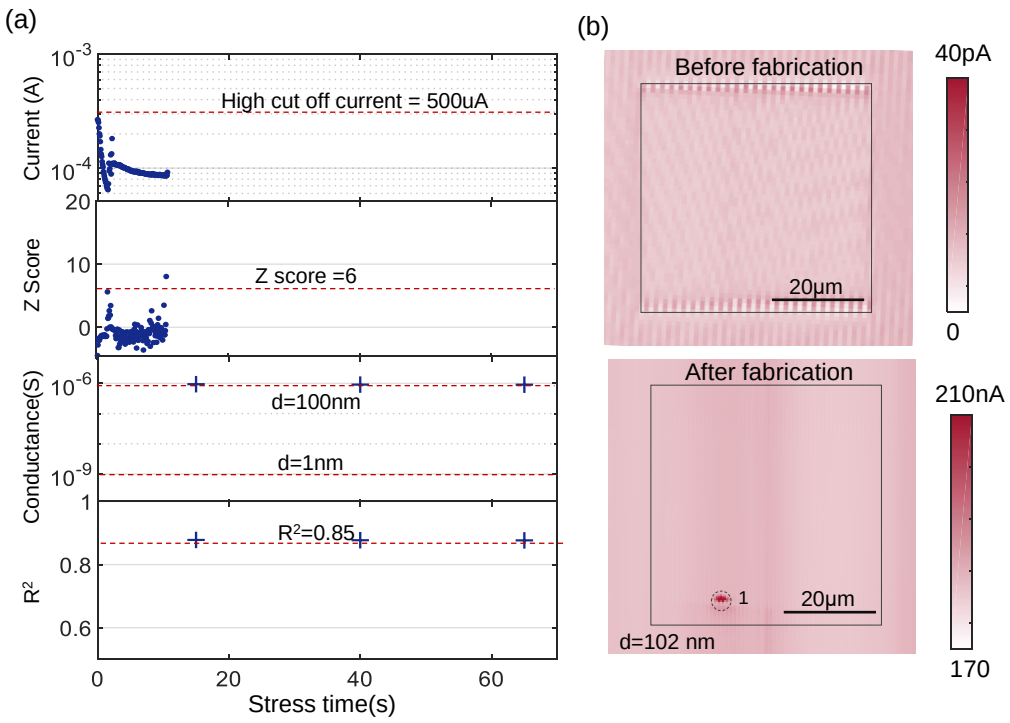


Figure S4. (a) A representative nanopore fabrication process at 1 V/nm initial electric field and 20 mW laser power. Nanopore was formed around 10 s. The nanopore diameter estimated by the conductance measurement was about 102 nm. (b) Scanned ionic current mapping before (top) and after (bottom) the nanopore fabrication. Ionic current mapping experiments were performed at 4 mW laser power and 100 mV voltage with 10 μm/s scanning speed.

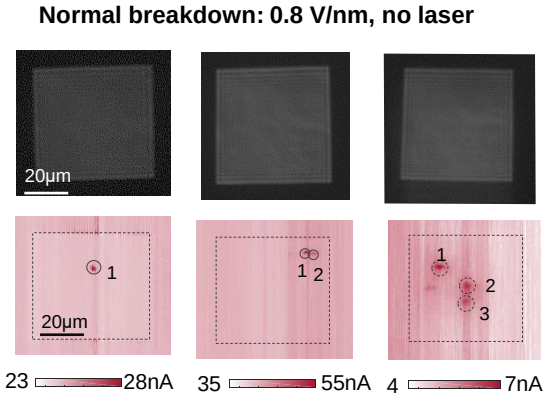


Figure S5. Normal breakdown at 0.8 V/nm without laser. The top figures are microscope images before fabrication. The bottom color maps are ionic current mapping results, which were performed at 4 mW laser power and 100 mV voltage with 10 μm/s scanning speed.

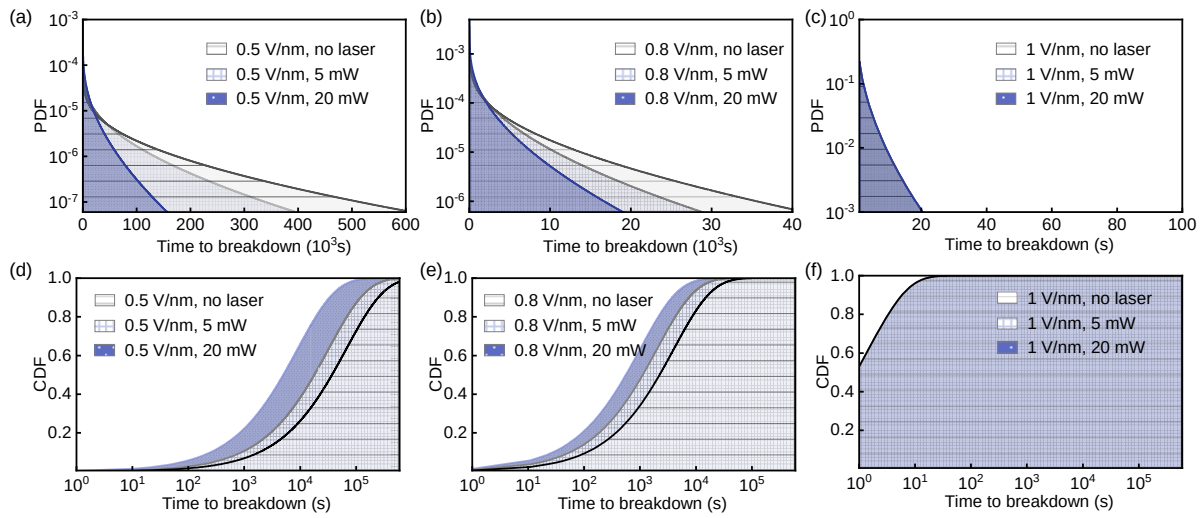


Figure S6. (a-c) Probability density function (PDF) and (d-f) Cumulative distribution function (CDF) of Weibull distribution of time to breakdown for normal and laser-assisted breakdown at different electric fields (0.5-1 V/nm) and laser powers (5-20 mW).

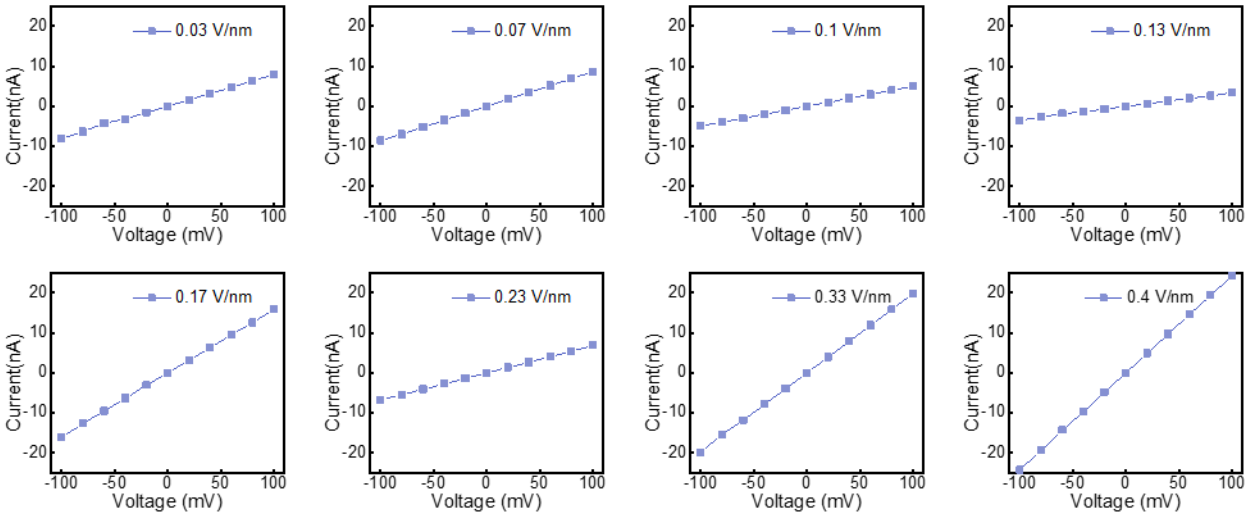


Figure S7. Conductance measurement. I-V curves of the nanopore fabricated by laser-assisted breakdown method at 20 mW laser and low electric field ranging from 0.03 V/nm to 0.4 V/nm. All measurements were performed in 1M KCl with 10mM Tris, and 1mM EDTA.

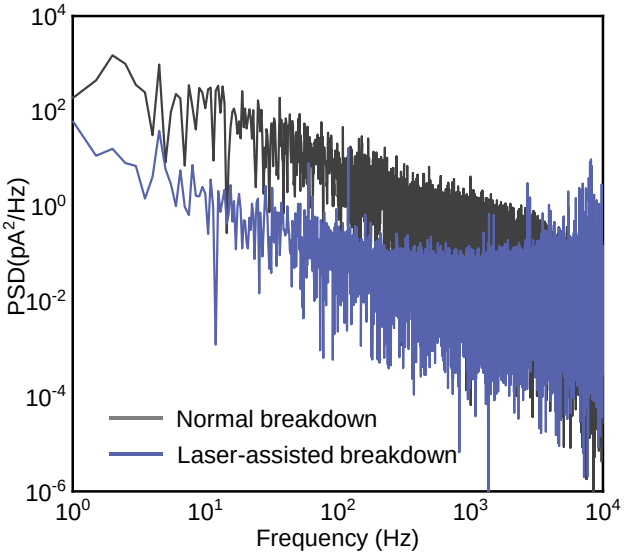


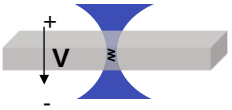
Figure S8. Measured power spectral density (PSD) of the normal breakdown and laser-assisted breakdown nanopore. The estimated pore diameter of normal breakdown methods and laser-assisted breakdown method are 9 nm and 10 nm respectively. All experiments were performed with 1 M KCl at 300 mV with a low-pass filter at 10 kHz.

Supporting Tables

Table S1. Parameters used for Arrhenius fitting in **Figure 2e**

Parameters	Meaning	Value	Unit
A	Arrhenius constant	31.6	Å/min
R	Gas constant	8.314×10^{-3}	kJ/mol/K
E_a	Activation energy	13.7	kJ/mol
b	Photothermal coefficient	8.06	K/mW
T_0	Room Temperature	293	K
P	Laser power	1-25	mW

Table S2. Comparison between normal breakdown and laser-assisted breakdown physics

	Normal Breakdown	Laser-assisted breakdown
		
Membrane thickness	d_0	$d(t) = d_0 - \mathrm{kt}$
Total number of the traps to reach the critical trap density	$N_n = D \times \mathrm{S} \times d_0$	$N_{la} = N_n \times \int_0^{t_{la}} \frac{d(t)}{t_{la} d_0} dt$
Electric field	$E_n = \frac{V}{d_0}$	$E_{la}(t) = \frac{V}{d(t)}$
Average breakdown time	$\int_0^{t_n} \frac{dt}{Be^{-\gamma E_n}} = 1$	$\int_0^{t_{la}} \frac{dt}{Be^{-\gamma E_{la}(t)}} = \frac{N_{la}}{N_n} = \int_0^{t_{la}} \frac{d(t)}{d_0} dt$

d_0: Initial membrane thickness; k: Etching rate; S: Area; D: Critical trap density; V: Voltage

Table S3. Parameters used in Figure 3a & Figure 3b

Parameters	Meaning	Value	Unit	Sources
k	Etching rate	2.88	Å/min	Arrhenius fitting result in Figure 2e
P	Laser power	50	mW	
V	Voltage	18	V	
d_0	Initial membrane thickness	30	nm	
B	Integration constant	5×10^{15}	s	Our experimental data[1]
γ	Field acceleration factor	38	nm/V	Published result[2]
β	Shape parameter	0.63	No Unit	Our experimental data[1]
λ_n	Average breakdown time (Normal)	24501	s	
λ_{la}	Average breakdown time (Laser-assisted)	1362	s	

Table S4. Parameters used in Figure 3c

Parameters	Meaning	Value	Unit	Sources
k	Etching rate	$Ae^{-\frac{E_a}{R(bP+T_0)}}$	Å/min	Arrhenius fitting result in Figure 2e
A	Arrhenius constant	31.6	Å/min	
R	Gas constant	8.314×10^{-3}	kJ/mol/K	
E_a	Activation energy	13.7	kJ/mol	
b	Photothermal coefficient	8.06	K/mW	
T_0	Room Temperature	293	K	
P	Laser power	1-50	mW	
V	Voltage	1-35	V	
d_0	Initial membrane thickness	30	nm	
B	Integration constant	5×10^{15}	s	Our experimental data[1]
γ	Field acceleration factor	38	nm/V	Published result[2]
β	Shape parameter	0.63	No unit	Our experimental data[1]

Supplementary References

S1. Roshan, K. A.; Tang, Z.; Guan, W., High fidelity moving Z-score based controlled breakdown fabrication of solid-state nanopore. *Nanotechnology* **2019,** *30*, 095502.

S2. Cramer, H.; Oliver, J.; Porter, R. In Lifetime of SiN capacitors determined from ramped voltage and constant voltage testing, 2*006 CS MANTECH Conference*, **2006**, 91-94.