Supporting Information for

Graphene Nanopore with a Self-Integrated Optical Antenna

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Methods

Graphene synthesis. Graphene was synthesized by chemical vapor deposition (CVD) on a 25 μ m thick copper foil¹ (99.8% Alfa Aesar, Ward Hill, MA). Briefly, copper foil was inserted into a quartz tube and heated to 1,000 °C while flowing 10 sccm H₂ at 150 mTorr. After annealing for 30 min, the gas mixture of 25 sccm CH₄ and 10 sccm H₂ at 520 mTorr was introduced for 20 min to synthesize graphene. Finally, the system was fast cooled to room temperature while flowing 20 sccm CH₄ at a pressure of under 330 mTorr.

Graphene transfer. After the synthesis, graphene was transferred to a Quantifoil holey carbon or an ultra-thin carbon membrane TEM grid (Electron Microscopy Sciences, PA) using a direct transfer method². We placed the TEM grid onto a graphene-covered copper foil with the carbon film side facing the graphene. Then a small amount of isopropyl alcohol (IPA) was dropped on to the sample and air-dried. An additional flattening step (prior to the IPA step) of the copper foil or the TEM grid was performed by sandwiching it between glass slides to ensure better adhesion. Finally, the sample was placed into a solution of sodium persulfate to etch the underlying copper foil and was then rinsed with deionized water.

Photothermal poration of graphene. Suspended graphene or graphene on an ultra-thin carbon membrane was porated through an air objective (×10, NA 0.3, WD 10 mm, UPLFLN; Olympus) with a Ti:sapphire laser (80 MHz repetition rate, 140 fs pulse width; Chameleon Ultra II, Coherent) on a laser-scanning microscope (Ultima; Prairie Technologies). The diameter of the laser spot is ~4 μ m. A typical setup utilized a frame size of 0.4 mm², and a laser spot dwell time of 10 μ s.

High resolution transmission electron microscope (TEM) analysis of graphene nanopore. The high-resolution TEM image was obtained with the TEAM 0.5 operated at

80 kV at the National Center for Electron Microscopy³. The microscope is equipped with image Cs aberration corrector and monochromator.

Darkfield imaging and spectrum analysis. Our microscopy system is composed of a Carl Zeiss Axiovert 200 inverted microscope with a darkfield condenser (NA 0.80-0.95, Nikon), a true-color digital camera (CoolSNAP cf; Roper Scientific, NJ), and a 300 mm focal-length and 300 grooves/mm monochromator (Acton Research, MA) with a 1024 × 256-pixel cooled spectrograph charge-coupled device (CCD) camera (Roper Scientific, NJ). The scattering images of gold nanoparticles were taken using a dry darkfield condenser with a 40× objective lens (NA 0.60, Carl Zeiss) and a true-color camera with a white light illumination (100 W halogen lamp). To perform the scattering spectrum analysis of gold nanoparticles, the scattered light was routed to the monochromator and spectrograph CCD (Acton SP2300 & PIXIS Model 256). An aperture was placed at the entrance slit of the monochromator (few-micron-wide aperture) to obtain a spectrum solely from a single nanoparticle in the region of interest.

Lambda phage DNA translocation experiment. Lambda (λ) DNA (48.50 kbp; New England BioLabs) molecules were dissolved in 0.5× Tris/Borate/EDTA (TBE) buffer with 10 mM NaCl and then fluorescently labeled with TOTO-1 (Molecular Probes) at a molar ratio of 4 bp per dye molecule. The length of the λ DNA molecule is ~20 µm after labeling⁴. The sample was diluted with the same buffer with 1% BSA (1 mg/ml; Sigma) to a concentration of 20 ng/ml before being injected into a polydimethylsiloxane (PDMS; Sylgard) device. The device was constructed with four components (bottom to top, see Figure S1): a standard microscope slide, a cured PDMS punched with two holes attached on top of the glass slide, an array of graphene nanopores with integrated gold optical antennae on the PDMS device sealed by epoxy adhesive, and a PDMS O-ring (inner diameter: 1 cm, height: 1 mm) attached on top of the PDMS device. The array of graphene nanopores with integrated with mitegrated with integrated with mitegrated with mitegrated gold optical antennae was fabricated with integrated gold optical antennae was fabricated with mitegrated gold optical antennae

photothermal poration (laser fluence of 2.5 mJ/cm²) of graphene/gold nanorods on an ultra-thin carbon membrane. The DNA sample and buffer with 1% BSA were injected to the bottom chamber and the top reservoir, respectively. We then connected the device with two Au electrodes (diameter: 0.1 mm; Sigma) to apply an electric field with a power supply (1–5 V; Keithley Instruments Inc.). We note that Au electrode might be less stable as compared with Ag-AgCl electrode; however, in our experimental setup, the Au electrode is used for driving DNA translocation and to allow short term fluorescent imaging versus electrical measurement of ionic current.

Fluorescence imaging of DNA translocation events. The device was mounted on a custom modified confocal microscope (OBX51S3; Prairie Technologies, WI) based on an upright microscope (BX-51WI; Olympus). The major parts of this microscope from Prairie Technologies include a x-y laser scanner (U-1002), a z-axis (focus) control automation system (ZM3) and a swept-field confocal scanner (SFC2). The DNA molecules were excited through a long working distance water immersion objective (×60, NA 0.9, WD 3.3mm, F.N. 26.5, UPLFLN; Olympus) with a solid-state diode laser (operating at 488 nm, ~50 mW output, polarized, Aurora-2; Prairie Technologies, WI) from the top of the device. The power after the objective was measured to be ~1 mW. The resulting fluorescence emission was collected by the same objective, selected by a 510-nm long-pass filter (Chroma Tech) and captured by an electron-multiplying CCD (QuantEM:512SC; Photometrics) with 2×2 pixel-binning and 100 ms exposure time.



Figure S1. Schematic illustration of graphene nanopore DNA translocation chip.

Estimation of Temperature Profile and Migration of Nanoparticles

Photothermal temperature profile estimation. The photothermal heat generation is calculated by

$$Q_{heat} = \int_{V} J \cdot E \, dV$$

where *J*, *E* and *V* are current density, electric field and volume, respectively. The femtosecond excitation on the nanorod generates a temperature profile repeatedly for multiple cycles. In the heating cycle, the maximum temperature is about 700 $^{\circ}$ C at a laser fluence of 2 mJ/cm².

Estimation of nanoparticle migration (i.e., anisotropic nanopore formation). Radiation force on the nanorod is calculated by

$$F_{rad} = \frac{1}{c} \oint \langle S \rangle \, dA$$

where $\langle S \rangle$ is time-averaged intensity, c is the speed of light and A is area. The radiation force can cause initial movement of the excited nanorod because it converts to a transverse force (F_{trans}) if the supporting substrate is not normal to the incident light (see Figure S2 for the schematic drawing). The following equation can be used to determine the nanoparticle migration distance.

$$m_{GNP} \cdot a = F_{trans} - F_{friction} = \{F_{rad} \cdot \sin \theta\} - \{F_{rad} \cdot \cos \theta \cdot \mu\}$$

where m_{GNP} is the mass of nanoparticle, *a* is acceleration, θ is the slant angle of substrate surface, $F_{friction}$ is a friction force, and μ is the coefficient of friction for the graphene/carbon substrate. A small angle θ and small coefficient of friction μ can result in 0.1 nm distance movement in each period. If the nanorod gradually melts during the 800 cycles of excitation, the radiation force based movement can be a dominant factor for the nanorod migration.



Figure S2. Schematic illustration of forces associated with the migration of nanoparticles.



Figure S3. Simulation of a gold nanorod temperature. Simulated temporal profile of temperature rising/cooling of a gold nanorod (GNR, 10 nm diameter by 38 nm length) after a single pulse laser illumination (fluence of 2 mJ/cm²). The substrate is a single layer graphene on a carbon membrane (c.a. 20 nm thickness). (Inset) Calculated peak temperature of GNR versus laser fluence.



Figure S4. Parallel light-to-heat sculpting of graphene nanopores. Each gold nanoparticle concentrates micron-sized light into nanoscale heated spots for parallel nanopore fabrication.



Figure S5. Atomic force microscope (AFM) image of multiple nanopores simultaneously formed by photon-to-heat sculpting. Nine nanopores with integrated optical antennae (marked with red arrows) are shown in Figure S5b (zoomed in image of dotted area in Figure S5a). Line scan of a nanopore is also shown in Figure S5c. Non-contact mode AFM scanning is performed.



Figure S6. A representative scanning electron microscope (SEM) image of gold nanorods on a graphene/carbon membrane prior to light illumination.



Figure S7. SEM image of nanopore (appearing black) with an integrated gold nanoantenna (appearing white) created on a suspended graphene membrane.



Figure S8. TEM image of the smallest width graphene nanopore. A narrowest nanopore width of ~2 nm (appearing white) is achieved by fine tuning the illumination condition.



Figure S9. SEM energy dispersive analysis (EDS) of gold optical antenna. SEM EDS results demonstrate that the optical antenna is composed of gold. Carbon and aluminum peaks are from the substrate and the sample holder, respectively; EDS taken from the substrate does not show a peak for gold but shows carbon and aluminum peaks. The inset shows a representative SEM image of the EDS data collection window (red box).



Figure S10. Atomic resolution TEM image of the edge nanostructure of a graphene nanopore. (a) Graphene hexagonal lattice (right) is shown with a nanopore (left). (b) Region 1 shows Fast Fourier Transform (FFT) of graphene hexagonal lattice. Nanopore area (Region 2, appearing white) shows no contrast, which is further supported by FFT. As the resolution limit of TEAM 0.5 microscope³ used to take this image is ~0.5 Å, the Region 2 does not contain any material/molecule that is larger than a 0.5 Å.



Figure S11. Uniform fluorescent intensity of the DNA fully-stretched by the applied electrical field during translocation through nanopore without an optical antenna. Inset shows a confocal scanning fluorescence image of λ DNA translocation through a nanopore without an optical antenna. Translocation membrane used in this control experiment (polycarbonate 0.2 µm; GE Water & Process Techn.) contributed to the auto-fluorescent background.

Fabrication Method	Smallest Pore Size	Throughput	Equipment Cost	Environment	References
Photothermal Poration	2 nm (Width)	High (Parallel)	Low (Optical Microscope, \$50,000-100,000 USD)	Vibration Free Environment	This Work
TEM Drilling	1~2 nm	Low (Sqeuencial)	High (High Voltage Gun, Vacuum, ~\$1,000,000 USD)	Electromagnetic Field Shielding & Vibration Free Environment	Refs 4-9 of manuscript
Focused Ion Beam (FIB) Drilling	10~20 nm	Low (Sqeuencial)	High (High Voltage Gun, Vacuum, ~\$500,000 USD)	Electromagnetic Field Shielding & Vibration Free Environment	Ref 8 of manuscript

Table S1. Comparison of nanopore fabrication method	ods.
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Supporting References

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