1. Device fabrication

To fabricate the silicon nitride membranes, we use 500 µm thick <100> p-type silicon (Si⁺) wafers with 100 nm of highly polished, low-stress amorphous silicon nitride (Si₃N₄) on both sides. These wafers were processed to produce many ~5 × 5 mm² chips, each with a 50 × 50 µm² region in its center where the Si₃N₄ membrane is freely suspended. The wafers are first coated on one side with a protective resist and on the other side with NR7 photoresist spun on at 3000 RPM for 42 seconds, and then baked at 115ºC for 3 minutes. The window mask is exposed to 365 nm light at 5 mW/cm² for 34 seconds and baked at 115ºC for 2 minutes. The wafer is developed in RD6 for 16 seconds, followed by a rinse with deionized water. To remove the silicon nitride, the wafer is then exposed to a SF₆ plasma etch in a Technics PeII-A Etcher at 50 W with a flow of 400 mtorr for 120 seconds. Finally, the wafer is exposed to a 1.5 M potassium hydroxide (KOH) wet etch at 130ºC. The KOH etches anisotropically through the silicon until the silicon nitride on the other side of the wafer is exposed, which takes approximately 18 hours. Once the etching is complete, the membrane window of 100 nm thick silicon nitride is further thinned to approximately 40 nm using another SF₆ plasma etch step.

Nanoelectrodes were patterned onto the window by electron beam lithography on an Elionix 7500-ELS, and 3 nm of nickel and 30 nm of gold were evaporated onto the devices.
Nickel was chosen as an adhesive layer for the small features because it leaves almost no debris in nanoscale gaps. Large metal features and contact pads were added using optical lithography followed by thermal evaporation of 3 nm of Cr and 100 nm of Au. Chips are allowed to outgas overnight after lithography steps to avoid TEM contamination. Twelve nanogaps were patterned per chip, with the gap size measured with a JEOL 2010F field-emission TEM to be 20-30 nm.

2. Additional characterization of the CdSe/ZnS nanocrystals

Nanocrystal size was determined from high-resolution TEM images (Figure S1) as the average of 50 nanocrystals, to be 5.2 ± 0.6 nm (Figure S2). Each nanocrystal was measured twice, with the measurements of the same nanocrystal roughly perpendicular to each other. These 100 measurements were averaged, giving a mean value of 5.2 nm with a standard deviation of 0.6 nm. However, there may be a slight underestimation due to the increased difficulty in discerning the ZnS shell against the carbon grid background.

The absorption and emission spectra of nanocrystals in toluene solution were recorded using SpectraSuite from Ocean Optics (Figure S3). The excitation wavelength for the emission data was provided using an Ocean Optics LS-450 with a 470 nm LED and filter. The light source for the absorption spectrum was an Ocean Optics LS-1 with a tungsten halogen bulb. The main excitonic peak was at 610 nm and the emission peak was at 638 nm. The reported quantum yield from Sigma-Aldrich is 30%.

Using the formula fitted by Yu et al., an absorption peak of 610 nm would correspond to a diameter of ~5.06 nm for a CdSe core nanocrystal. It has been shown that adding a ZnS shell not only broadens, but also redshifts the absorption peak, and the size of the redshift depends on the size of the nanocrystal. We estimate a redshift of ~5 nm, so that the absorption peak for our CdSe core should be 605 nm. From Yu et al., the core diameter of our CdSe nanocrystals is ~4.81 nm. It should be noted that had we not taken into account the redshift caused by the shell, we would have overestimated the core size by ~0.25 nm. Knowing that the core radius is 2.4 nm and the actual nanocrystal radius, determined by TEM, is 2.6 nm, we find that the shell is ~0.2 nm, which is approximately one monolayer.
Figure S1. High-resolution TEM images of CdSe/ZnS nanocrystals on a carbon grid.

Figure S2. Histogram of 50 nanoparticles, each measured twice from TEM images.
3. Effect of annealing

The percentage of devices that had measurable photocurrent increased with annealing temperature $T_a$. For $T_a = 423K$ the yield was 44%, for $T_a = 498K$ the yield was 66%, and for $T_a = 573K$ all devices showed photocurrent response. In devices that had photocurrent above the noise floor (0.03 pA at 295K and 0.15 pA at 78K), increasing the annealing temperature from 423K to 498K increased the observed photocurrent by 20 times on average. Above 498K, there was no measurable change in photocurrent magnitude or response characteristics. All data discussed were taken from 17 active nanogaps out of 20 total that were annealed at either 498K or 573K.

4. Dark current on bare device and device with nanocrystals

Dark current was measured on all nanogaps prior to any nanocrystal deposition, prior to any photocurrent measurements, and over the course of several months as devices were thermally cycled many times. Dark current was below the noise floor of our setup for 70% of devices measured. In Figure S4, we show examples of I-V characteristics for a bare nanogap.
measured at room temperature and for nanogaps with nanocrystals that have been annealed and measured at 78K and 295K.

Figure S4. Representative I-V dark current curves for a bare device, and devices with nanocrystals annealed up to 573K and measured at 295K and 78K. More than 70% of devices showed no measurable dark current, making them primary photodetectors.

Less than ~30% of nanogaps, only those annealed at 573K, showed a very small dark current (~0.16 pA at 2V), 2-3 orders of magnitude smaller than the corresponding photocurrent. The dark current increases exponentially with voltage and can be empirically fitted to an exponential form $I_{\text{dark}} = \frac{V_o}{R_o} e^{\frac{V}{V_o}}$, where $R_o \sim 2 \times 10^{14} \Omega$ and $V_o = 0.7 \ V$ are the characteristic resistance and voltage (Figure S5). This is in agreement with previously reported dark current measurements on micron-scale nanocrystal arrays. Consequently, because there is no clear threshold of the dark current, this also implies that there is no intrinsic difference between primary and secondary photodetectors in these systems. Whether a photodetector is labeled “primary” or “secondary” is determined by the noise floor of the measurement setup.
**Figure S5.** I-V curve for one of the few devices with measurable dark current.

Figure S6 shows the temperature dependence of the dark current, written as the zero-bias conductance $G$ vs. $1/T$, which is representative for the few devices that exhibited measurable dark current.

**Figure S6.** Sample Arrhenius plot with calculated activation energy.
The dark current is thermally activated and conductance was found to scale as $G \sim e^{\frac{E_a}{k_B T}}$. We have measured a range of activation energies from ~70-230 meV, consistent with previously published results.\textsuperscript{4}

5. Wavelength dependence of photocurrent

Examples of I-V sweeps at illumination wavelengths of 473 nm, 532 nm, and 650 nm and the positions of these laser excitation wavelengths on the absorption vs. wavelength curve are shown in Figure S7.

![Figure S7. Representative photocurrent vs. voltage curves for 650 nm (red), 532 nm (green) and 473 nm (blue) laser excitations. Inset: Absorption and emission intensities vs. wavelength for CdSe/ZnS nanocrystals in solution. The blue, green, and red circles indicate the positions of the excitation wavelengths with respect to the absorption curve.](image)

6. Statistics of photocurrent

Nanocrystal films at the nanoscale show some amount of nonuniformity because of the small number of nanocrystals in the gap area. Figure S8 shows the distribution of photocurrent magnitudes for all our measured data using a 532 nm laser.
Figure S8. Distribution of photocurrent magnitudes for nanogap devices illuminated with 532 nm light. Histogram includes data from all treatments.

7. Representative images of a measured device

Figure S9 shows an optical image of an entire chip after nanocrystal deposition, annealing, and photocurrent measurements. Figure S10 shows two TEM images of different nanogaps after nanocrystal deposition, annealing, and photocurrent measurements. The nanocrystal film in the gap area appears blurred due to the thickness of the film.

Figure S9. Optical image of a device with annealed nanocrystals after measurement.
Figure S10. TEM images of two different nanogaps on the same chip after measurements with nanocrystals annealed at 498K.

8. Robustness of ratio $R$ adjustment

For the initial I-V measurements of the devices taken using a 532 nm laser after several days without measurements, Figure S11 shows the measured photocurrent ratio $R$ was in the approximate range of 1 to 10.

Figure S11. Distribution of $R$ values for nanogap devices illuminated with 532 nm light. Histogram includes data from all treatments.
Illumination with a 650 nm laser produced photocurrent at room temperature (0.01-2.9 pA, with a mean of 0.36 pA) but lower photocurrent at low temperature (0.01-0.7 pA, with a mean of ~0.17 pA), yielding overall smaller ratios $R$ in the range of 0.1 to 2. These two ratio populations are shown in a histogram in Figure S12. The smaller ratio $R$ values for 650 nm versus 532 nm excitation can be understood by recalling the change in the absorption peak of these nanocrystals with temperature. At room temperature, the peak is thermally broadened which allows an overlap between the laser excitation and the absorption peak. The peak at 610 nm is thermally narrowed and blueshifted at low temperature because of the temperature dependence of the Stokes shift, which reduces the overlap of the laser excitation and the peak, causing photocurrent to be lower. The photocurrent from illumination at 980 nm was also measured, but was found to be negligible as expected due to the energy mismatch between the nanocrystal bandgap and the energy of the incident photons.

![Figure S12](image)

**Figure S12.** Histogram of the ratio $R = I_{78K}/I_{295K}$, with data taken from comparable treatments, for two laser excitation energies corresponding to excitation wavelengths of 532 nm and 650 nm. Higher illumination energy (532 nm) results in larger $R$, with an average $R$ of 2.8. The average $R$ for the 650 nm excitation is 0.7.
We find that using the laser voltage treatment to increase the relative photocurrent ratio $R = I_{78K}/I_{295K}$, or using the dark voltage treatment to decrease $R$, is a robust and repeatable process. Nanogap devices can be cycled to high and low $R$ values many times without the effect losing potency. We measured our devices for several months and continued to observe the same reversible behavior. Table S1 shows the relative photocurrent ratio $R$ of several nanogaps, and its changing value after laser or dark voltage treatments. This data was taken with a 650 nm laser.

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<th>$R$ after dark voltage treatment</th>
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Table S1. Relative photocurrent ratios of the low- and room-temperature photocurrents, $R = I_{78K}/I_{295K}$ for several nanogap devices on a single chip, illuminated with 650 nm light, increasing or decreasing with different treatments.

9. Ratio $R$ inversion between $R < 1$ and $R > 1$

The temperature dependence of the photocurrent can be repeatedly reversed in a single nanogap device to yield a temperature-decreasing or temperature-increasing photocurrent. This is illustrated by one nanogap in Figure S13 for a range of laser intensities used.
Figure S13. Measurements of photocurrent versus laser intensity (a) before and (b) after a dark voltage treatment of a single nanogap which show the ratio $R = \frac{I_{78K}}{I_{295K}}$ switching from (a) $R > 1$ when $I_{78K}$ (blue) > $I_{295K}$ (red) to (b) $R < 1$ when $I_{78K}$ (blue) < $I_{295K}$ (red) for all laser intensities used.
References


