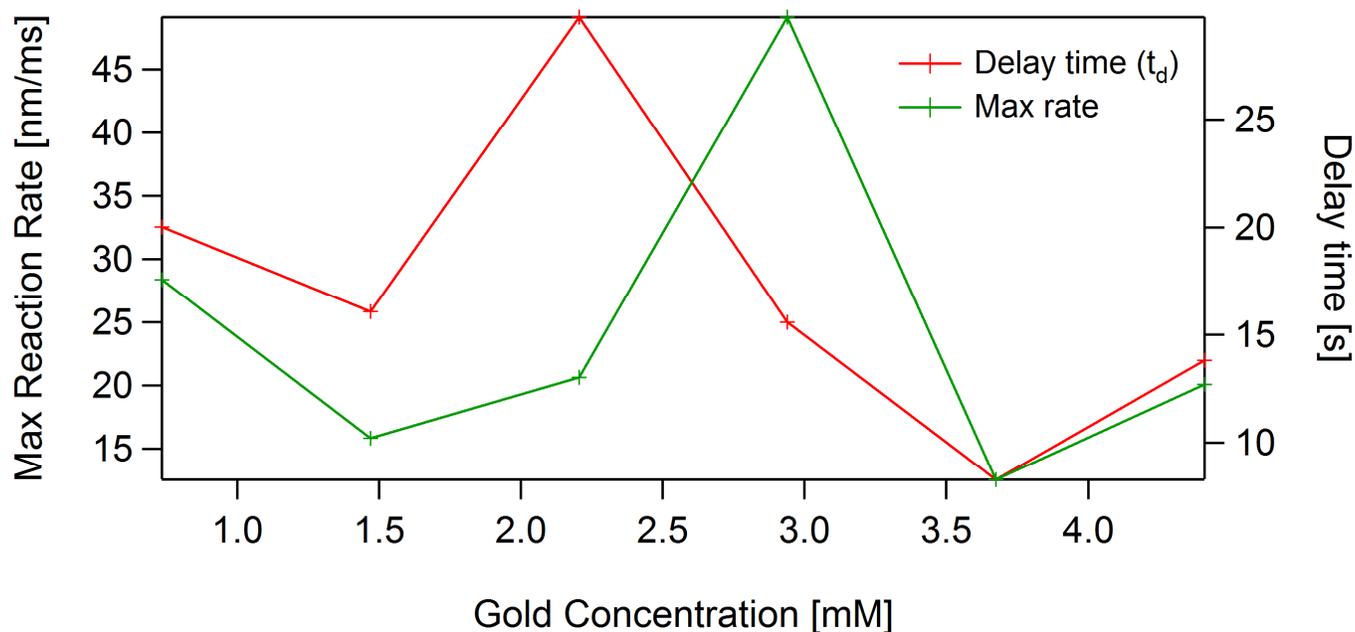


# Electrically controlled nanoparticle synthesis inside nanopores

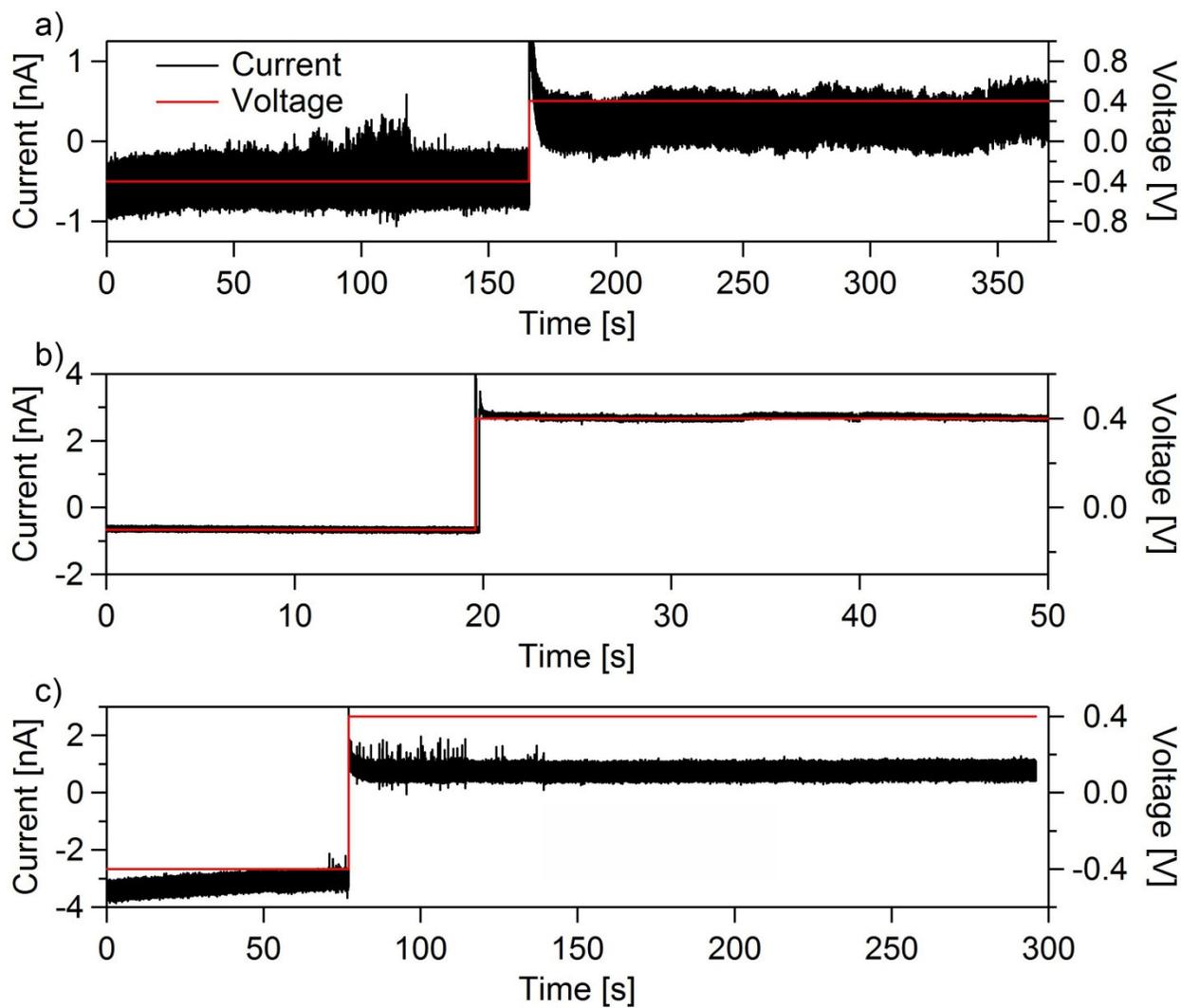
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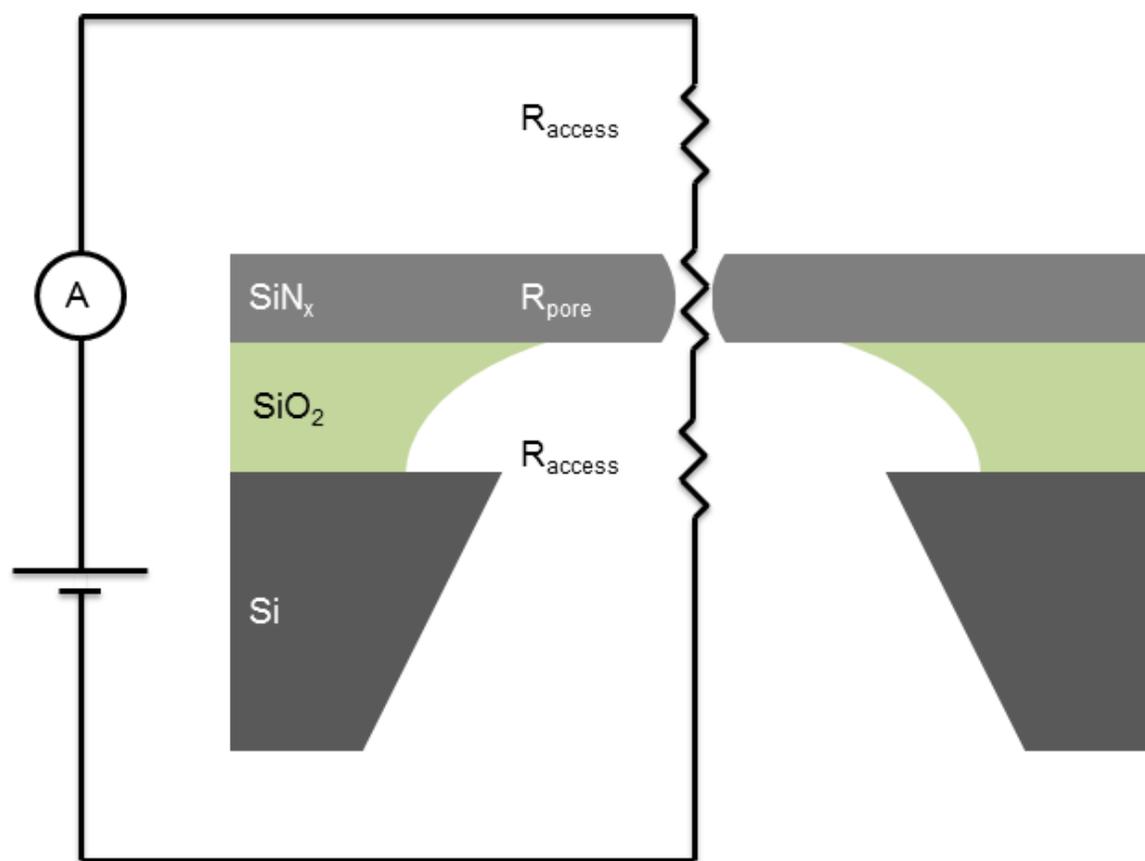
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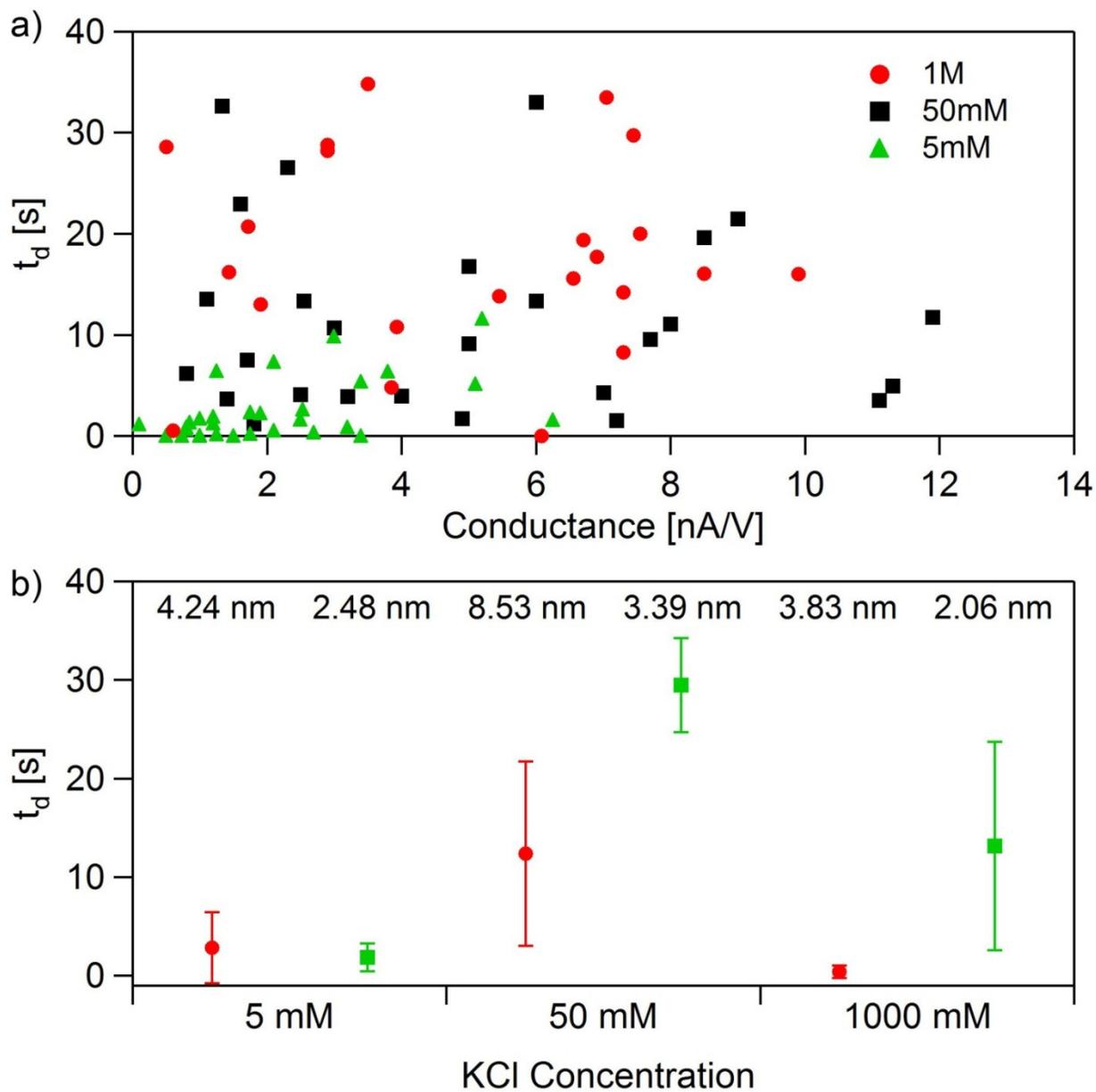
**FIGURE S1** Delay time ( $t_d$ , red) and maximum reaction rate (green) vs. gold chloride concentration. These experiments were carried out on a 5 nm diameter pore in 5 mM KCl solution with 0.0312 mM hydrazine concentration. We chose to carry out all further experiments at a gold chloride concentration of 2.94 mM, as this concentration shows the fastest particle formation, i.e., the fastest reaction rate and one of the lowest delay times before particle formation begins.



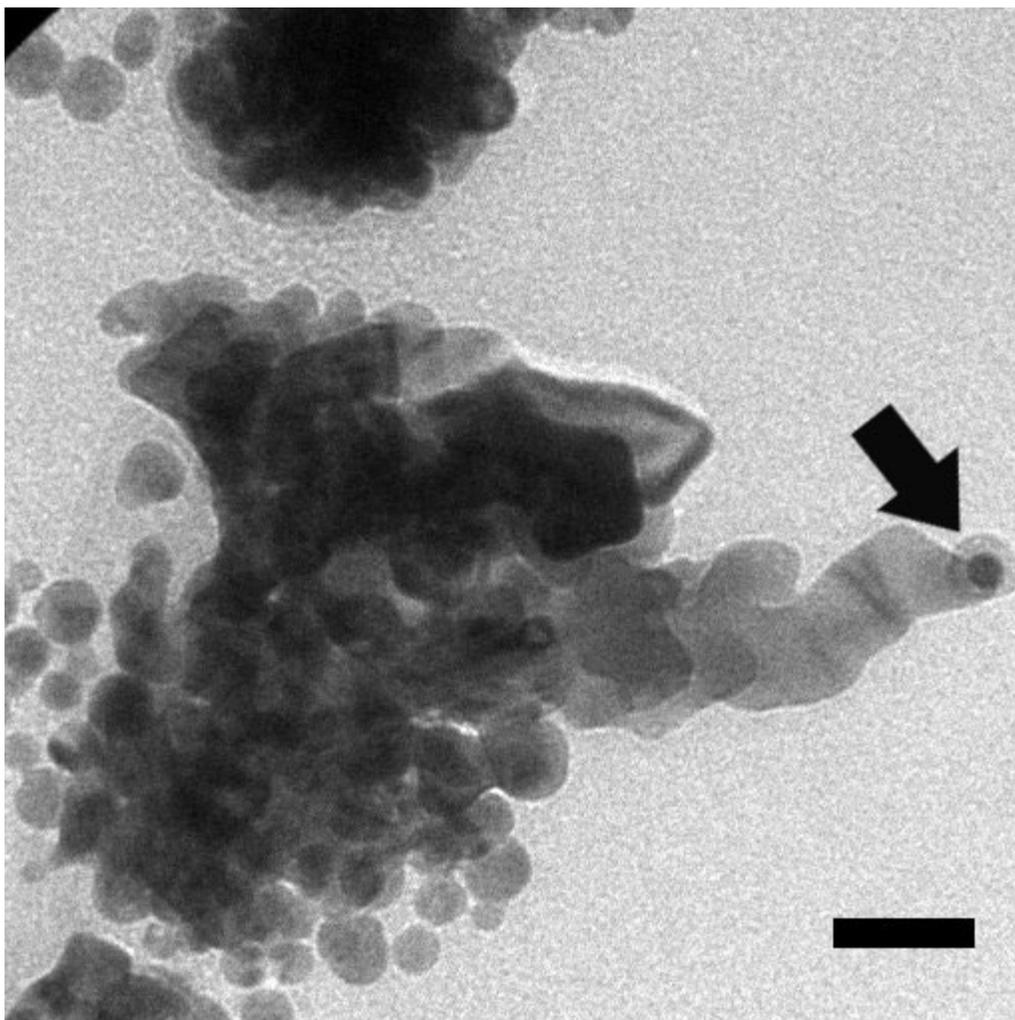
**FIGURE S2.** Control experiment graphs of current vs. time and voltage vs. time for a) hydrazine, b) gold, and c) gold/ $\alpha$ -lipoic acid complex. The conductivity remains approximately the same after the voltage is changed, indicating that the pore remains open.



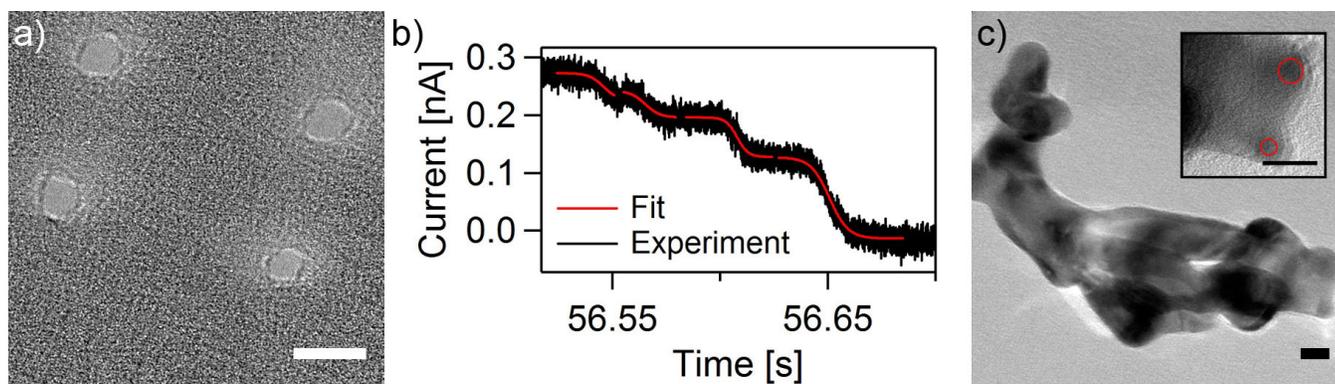
**FIGURE S3.** Schematic of circuitry in our system



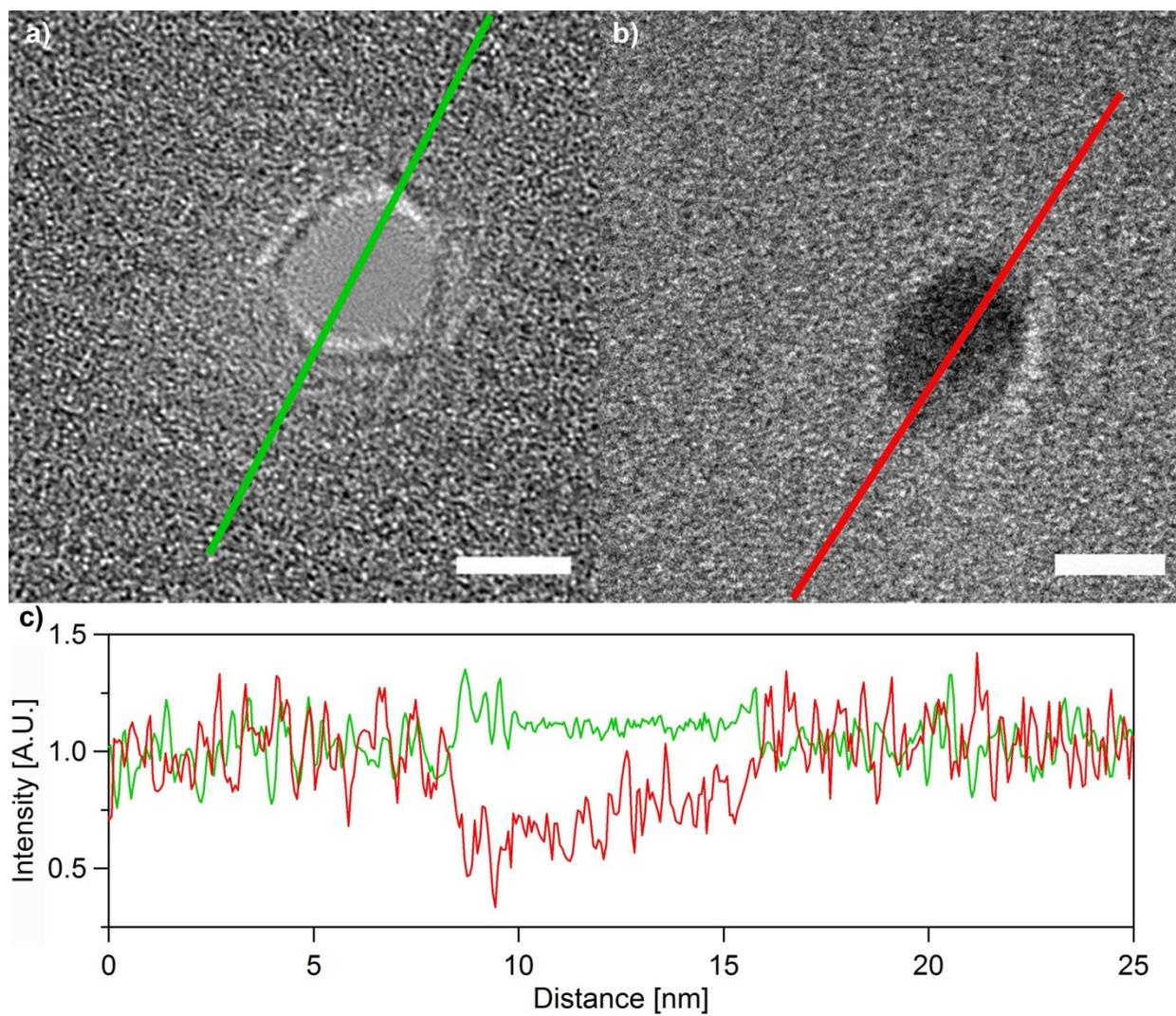
**FIGURE S4.** Delay time dependence on pore conductance and KCl concentration. We examined the effect of pore conductance (pore conductance is proportional to pore size) on  $t_d$  values. (a) Scatter plot of  $t_d$  vs. pore conductance, showing no clear correlation. (b) Average from 5 to 10 experiments of  $t_d$  for two pores of different sizes at each KCl concentration, showing no clear correlation. Pore size is given at the top of panel b.



**FIGURE S5.** Transmission electron micrograph of gold formed in 1M KCl. The relatively long delay time,  $t_d$ , before the pore closes allows additional reagent to traverse the pore and react, resulting in aggregate gold around the nanopore (indicated by the arrow). Scale bar is 20 nm.



**FIGURE S6.** Particle formation events in an experiment with multiple nanopores on a single chip. Experiment was done on an array of four nanopores shown in the TEM in (a) in 50 mM KCl solution without  $\alpha$ -lipoic acid. (b) Ion current trace shows stepwise reduction in the current and corresponding fits of four distinguishable formation curves. Voltage polarity was switched at  $t = 13$  s. (c) TEM after particle formation. In addition to Au formation in the pores (darker regions in the TEM image), we observe that Au forms outside of pores as well. Inset is a zoomed in image of the pores, with their locations circled in red. All scale bars are 10 nm. Note that in the absence of  $\alpha$ -lipoic acid additional gold formed outside the pore region. We suspect the formation of the four particles is correlated. This is supported by the gold connecting the four pores, as well as the  $t_d$  of the four events having much less variation than observed in Figure 4. Future studies could include device designs where nanopores are individually controlled by electric fields.



**FIGURE S7.** TEM of a pore (a) before and (b) after particle formation. (c) Profile of the intensity of the TEM images taken along red and green lines as marked. Particle was formed in 50 mM KCl with  $\alpha$ -lipoic acid.