Supplementary Information

A hydrophobic entrance enhances ion current rectification and induces dewetting in asymmetric nanopores

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1. Summary of all single PET nanopores that were sputtered with a layer of gold followed by chemisorption of C10 or C18 thiols.

Table S1. Transport properties of single nanopores with a hydrophobic layer. The pores were studied in the voltage range (-5V, +5V). The last column contains threshold voltages which opened the pore for ionic transport. The voltage thresholds are typically averages of two scans.

Au thickness (nm) and type of thiols used	Tip size, Base size in (nm)	Reversal of rectification at pH 3			Closure at pH 3			Existence of fluctuating ion current signals with threshold voltages in V: negative voltage/positive voltage threshold		
		1 M	0.1 M	10 mM	1 M	0.1 M	10 mM	1 M	0.1 M	10 mM
10, C10	9, 213				X	X	X			
10, C10	10,196			X	X	X				
10, C10	11, 175				X	X	X			
10, C10	12, 170				X	X	X	X -0.8 / +1.4	X -0.8 / +2.6	
15, C10	11, 151		X	X						
15, C10	11, 350				X	X	X	X -2.1 / +2.6	X -0.3 / +1.0	X -2.9 / +3.1
15, C10	13, 170						X		X open / +2.5	
15, C10	13, 440				X	X	X			
15, C10	15, 570					X	X			X open / +3.8
22.5, C18	16, 170						X	X -1.4 / +2.4		

22.5, C18	16, 600		X		X		X	X -1.7 / n/a	X -1.7 / +3.6	
22.5, C18	17, 210							X -0.8 / n/a	X -1.8 / +2.0	
22.5, C18	17, 820			X			X			X n/a, / +4.2
22.5, C18	18, 160							X -0.6 /+ 1.0	X -0.9 / +0.7	
22.5, C18	21, 250	X	X		X	X*	X	X -1.3 / + 0.6	X -2.2 / +2.0	X -5.0 / n/a
22.5, C18	22, 350		X	X						
22.5, C18	24, 570	X	X	X						
22.5, C18	28, 220				X*	X*	X			
22.5, C18	33, 290						X*			

X* - Indicates partial effect, i.e. the pore did not close fully, however the conductance was significantly reduced, at least by an order of magnitude, compared to recordings at pH 8

- n/a - the pore remained closed for the whole studied range of voltage at one polarity.

- 'open' - the pore remained conductive for one voltage polarity

2. Numerical modeling of ionic concentrations and current-voltage curve in nanopores with and without gold layer.

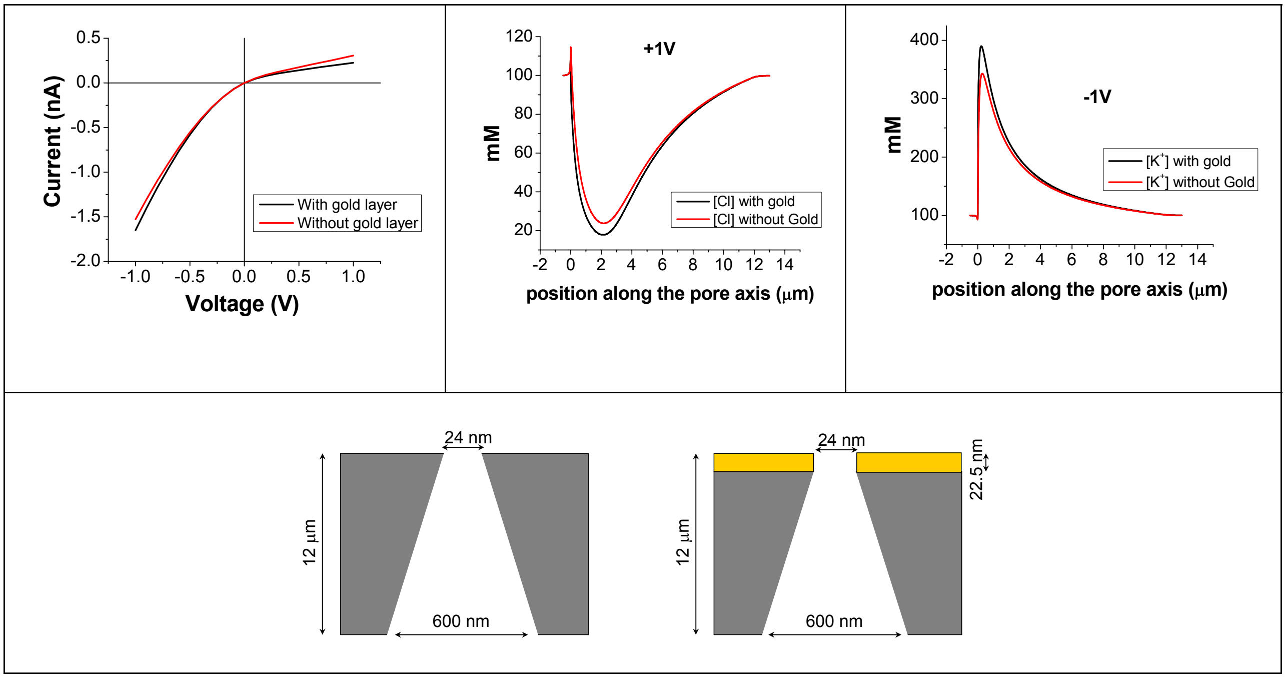


Figure S1. Results from numerical modeling of ion currents and ionic concentrations in a single nanopore with and without a gold layer. Poisson-Nernst-Planck equations were solved using the commercial software COMSOL.[1,2,3] (top, left) current-voltage curves, (top, middle) concentration of Cl^- ions, and (top, right) concentration of K^+ ions along the pore axis. The bottom row shows schemes of the structures that were modeled. The surface charge density of the gold layer was -0.32 C/m^2; for the polymer surface -0.16 C/m^2. The bulk concentration of KCl was 0.1 M.

The modeling qualitatively agrees with the experimental observations: adding a gold layer to the pore entrance increases ion current rectification and ionic concentrations at the pore tip. The experimentally observed effects are however stronger than suggested by the modeling. We think it can be due to possible changes in the geometry at the pore opening caused by the gold sputtering.

3. Example of C18 thiol modified nanopore that at pH 8 rectified less than before sputtering a gold layer.

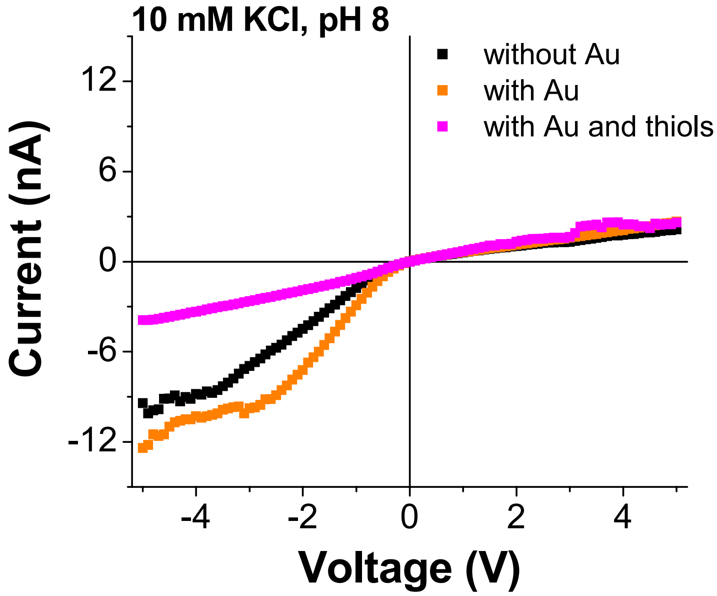
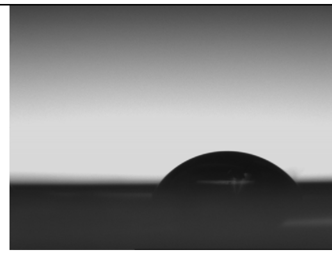
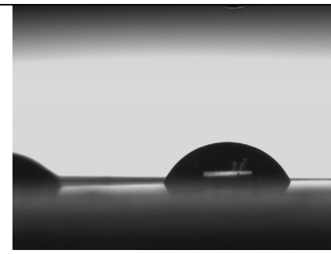
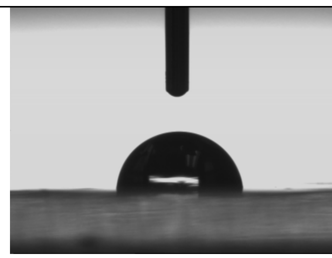
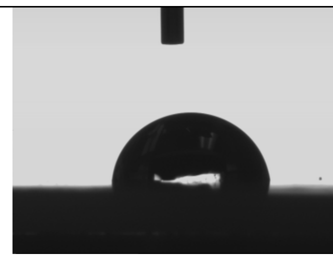
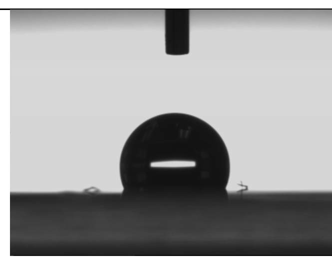
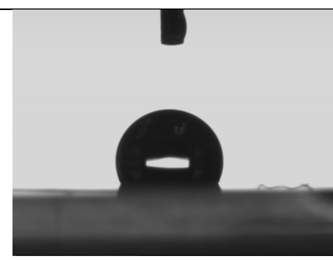
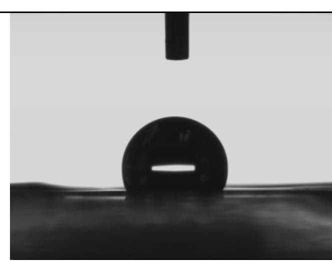
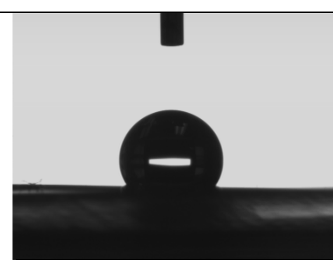


Figure S2. Ion current through a single nanopore before and after depositing a 22.5 nm thick gold layer, followed by chemisorption of hydrophobic thiols C18. The recordings were performed in 0.1 M KCl pH 8.

4. Contact angle measurements

Table S2. Contact angle measurements of the same surfaces which were examined in Table 1 of the main manuscript but determined at 100 mM KCl, pH 3 and pH 8.

Type of Surface	Contact angle in 100 mM KCl, pH 8	Contact angle in 100 mM KCl, pH 3
Unmodified PET	 54 ± 2°	 67 ± 5°
A gold surface	 85 ± 7°	 88 ± 9°
A gold surface with C10 thiols	 115 ± 2°	 112 ± 2°
A gold surface with C18 thiols	 105 ± 10°	 118 ± 2°

References

1. I. Vlassiouk, T. Kozel and Z.S. Siwy, *J. Am. Chem. Soc.*, 2009, **131**, 8211.
2. I. Vlassiouk, S. Smirnov and Z.S. Siwy, *ACS Nano*, 2008, **2**, 1589.
3. M.R. Powell, I. Vlassiouk, C. Martens and Z.S. Siwy, *Phys. Rev. Lett.*, 2009, **103**, 248104.