Electronic Supplementary Material (ESI) for Analyst.

Experimental and Finite Element Method Studies for Femtomolar Cobalt Ions Detection by a DHI Modified Nanochannel

Supporting Information

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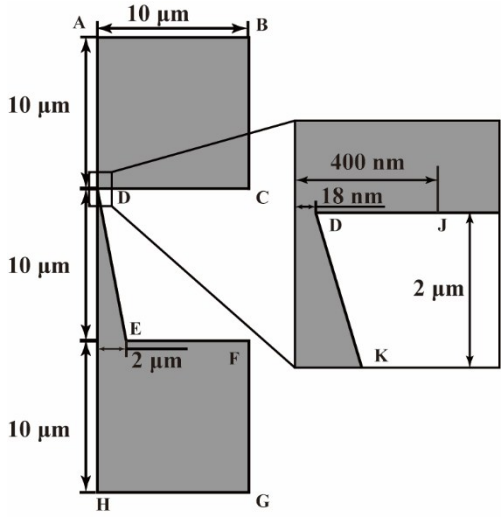

Scheme S1. Geometry of a 36 nm diameter conical nanopore. (A) to (K) shows the boundary between different conditions and details shown in Table S1.

Table S1. Details of boundary conditions used in modeling

Surface	Poisson	Nernst-Planck	Navier-Stocks
AB	Constant potential $\phi = 0$	Constant concentration $\mathbf{c}_K = \mathbf{c}_{Cl} = 1$ M $\mathbf{c}_{Co} = 1$ nM	Constant pressure p = 0 no viscous stress $n[\mu(\nabla u + (\nabla u)^T)] = 0$
GH	Constant potential $\phi = \mathbf{V}$	Constant concentration $\mathbf{c}_K = \mathbf{c}_{Cl} = 1$ M $\mathbf{c}_{Co} = 0$ M	Constant pressure $\mathbf{p} = 0$ no viscous stress $n[\mu(\nabla u + (\nabla u)^T)] = 0$
BC, CJ, KE, EF, FG	Zero charge $-\mathbf{n}\cdot(\varepsilon\nabla\phi) = 0$	No flux $-\mathbf{n}\cdot\mathbf{N}_i = 0$	No slip $\mathbf{u} = 0$
JD, DK	-0.012 C/m^2 $-\mathbf{n}\cdot(\varepsilon\nabla\phi) = \sigma_w$	No flux $-\mathbf{n}\cdot\mathbf{N}_i = 0$	No slip $\mathbf{u} = 0$
AH	axial symmetry	axial symmetry	axial symmetry

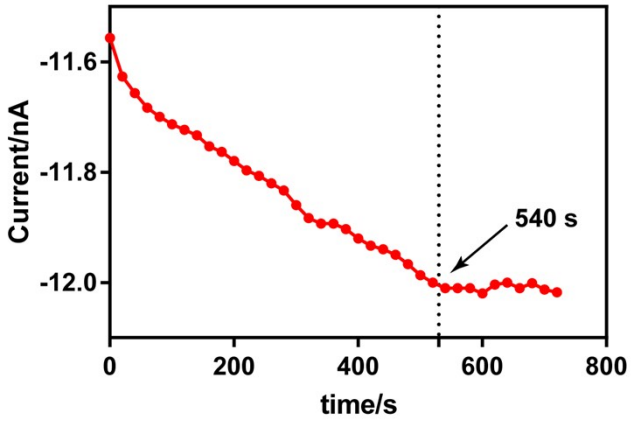

Figure S1. The effect of Co^{2+} recognition quite time on the detection current of 20 μM of Co^{2+} in a DHI modified nanopore with 1 M KCl aqueous electrolyte solution (pH = 7).

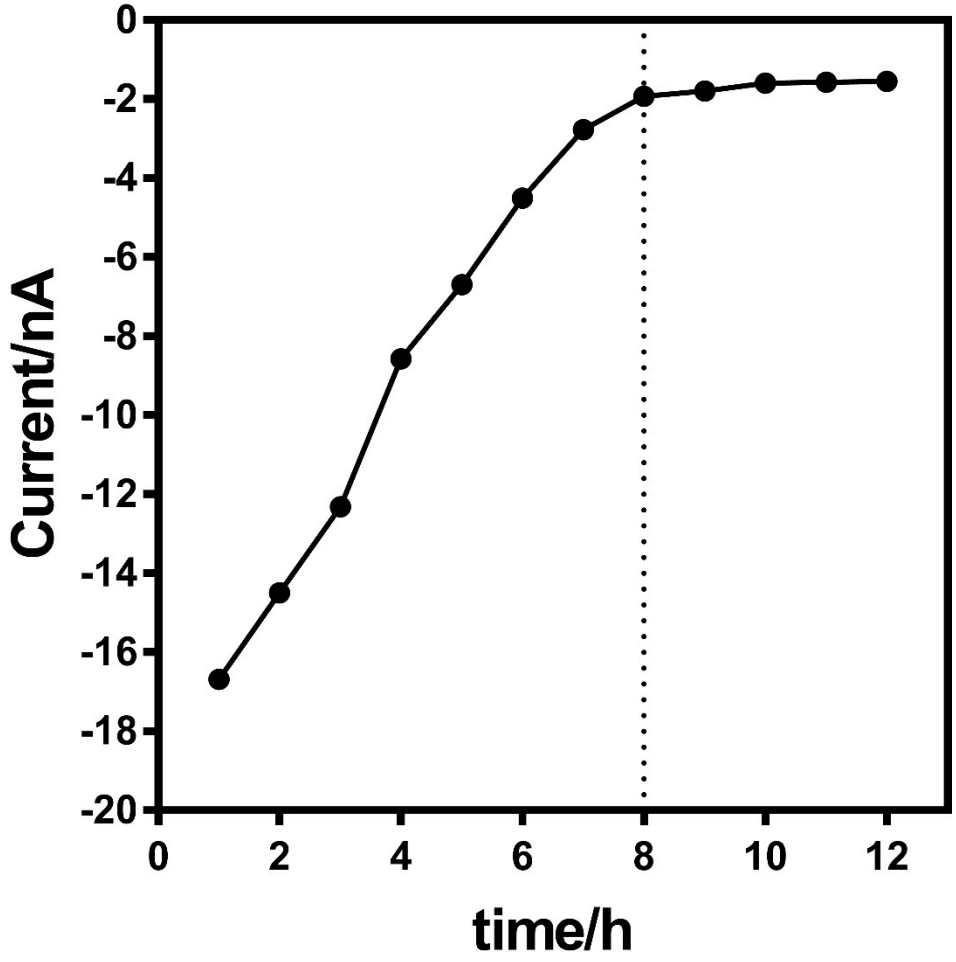

Figure S2. Negative ionic current trace with the change of immobilization time.

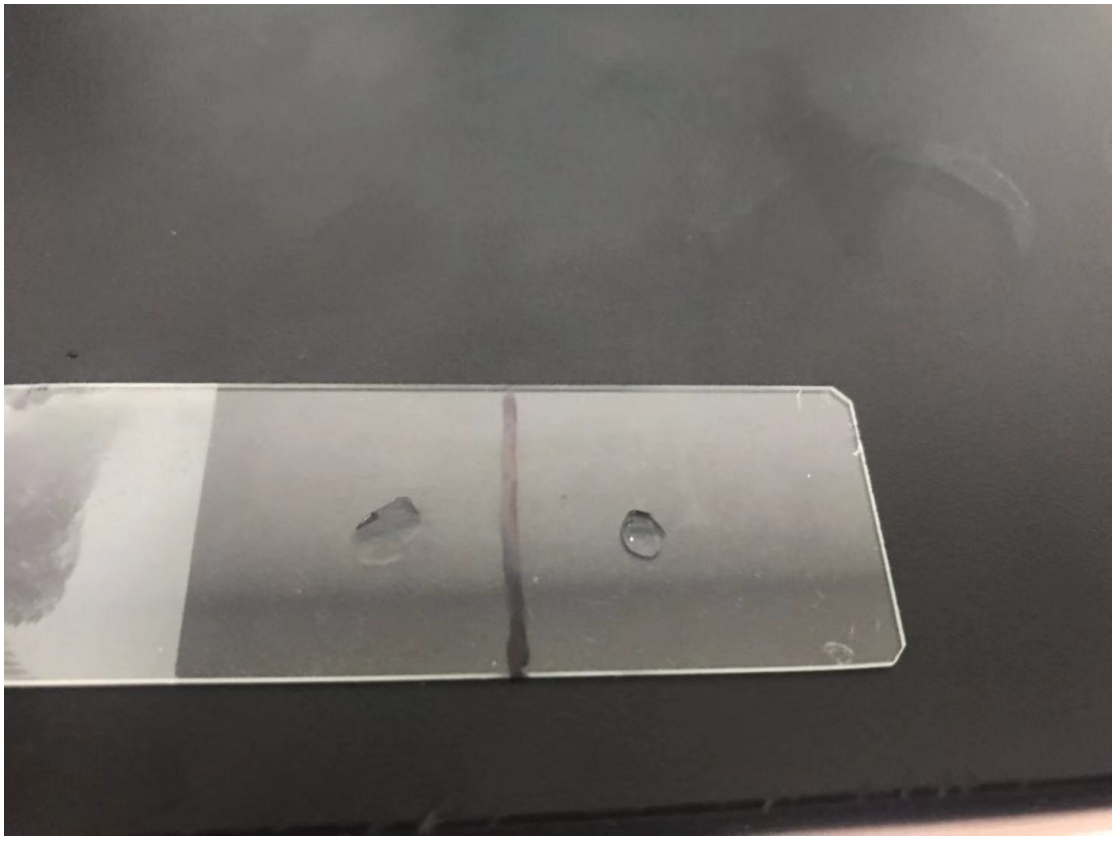

Figure S3. Wetting conditions of DHI modified quartz plate before (right) and after (left) 1 mM CoCl2 solution treating.

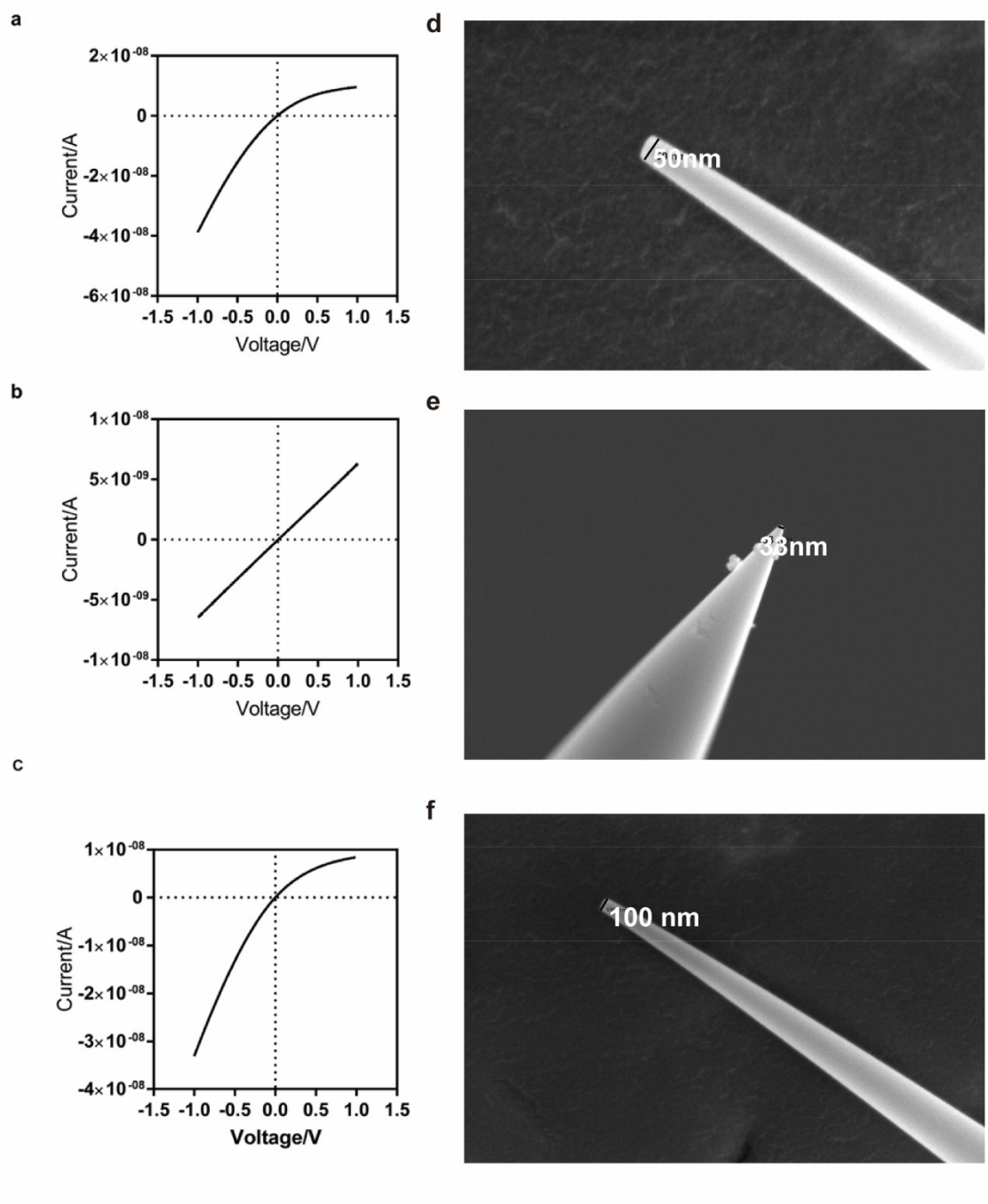

Figure S4. I-V curve of unmodified nanopore which produced by HEAT = 550 (a), HEAT = 675 (b) and HEAT = 575 (c) whose diameters were calculated as ~ 60 nm, ~ 12 nm and ~30nm, respectively. (d) to (f) are their SEM results, respectively.

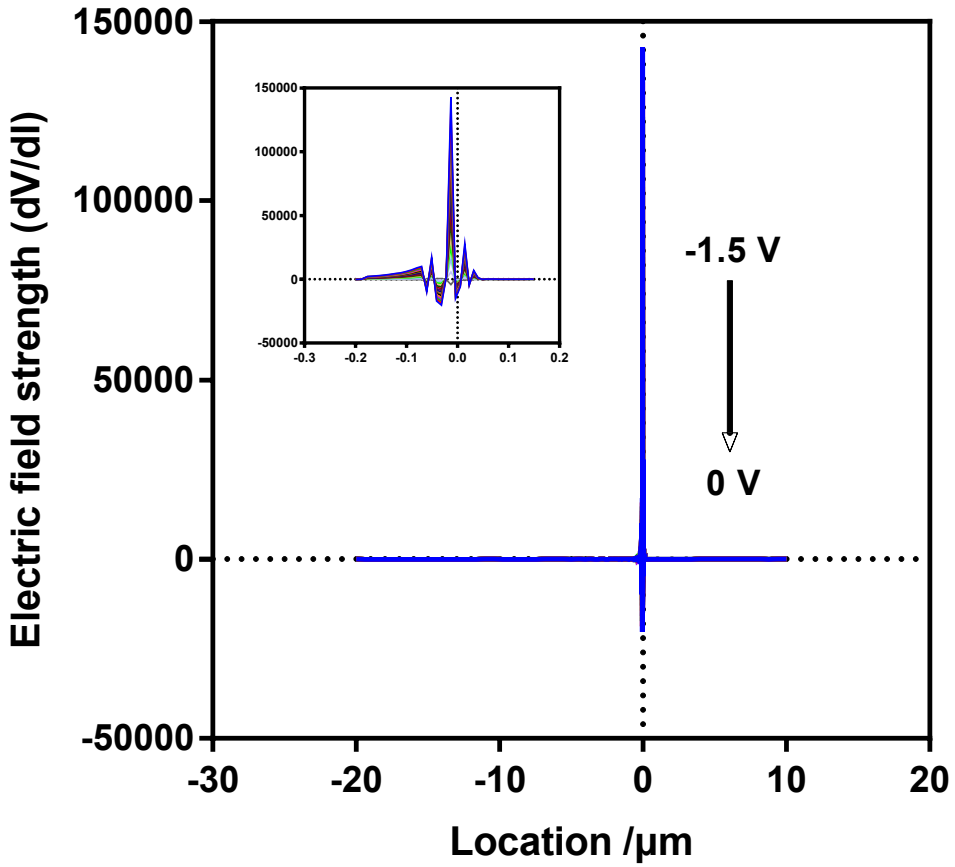

Figure S5. Voltage drop along the asymmetric axis under different applied voltage.

Table S2. Results of linear fitting for reponses ionic current in alkaline electrolyte

Potiential (V)	Slope (nA/lgCo^{2+})	Intercept (nA)	Goodness for linear fitting (R^2)
-1	-0.4917	-8.843	0.9913
-0.8	-0.3985	-7.814	0.9837
-0.6	-0.299	-6.232	0.9696
-0.4	-0.2032	-4.322	0.9551
-0.2	-0.1035	-2.245	0.9404

Table S3. Comparison of analytical methods for the detection of Co^{2+}

Method	Linear range (nM)	Limit of detection (nM)	References
Microextraction method	0.6440 – 59.43	0.06452	[1]
ICP-MS	33.93 – 1696	3.394	[2]
Fluorescence spectrometry	848.4 – 20362	101.8	[3]
Fluorescence spectrometry	10 – 800	2.4	[4]
Modified Nanopore	2.000×10^{-5} – 2.000×10^{5}	9.402×10^{-7}	This work

Table S4. Results of the detection of Co^{2+} in tap water

Sample	Co^{2+} added (nM)	Co^{2+} measured (nM)	Recovery (%)	RSD (%, N = 5)
1	0	\	\	1.76
2	1	0.96	96.0	2.99
3	10	9.84	98.4	1.80
4	100	100.19	100.19	4.01

1. P. Berton and R. G. Wuilloud, *Analytica chimica acta*, 2010, **662**, 155-162.
2. A. Martín-Cameán, A. Jos, A. Calleja, F. Gil, A. Iglesias-Linares, E. Solano and A. M. Cameán, *Microchemical Journal*, 2014, **114**, 73-79.
3. C. Zeng, Y. Jia, Y.-I. Lee, X. Hou and L. Wu, *Microchemical Journal*, 2012, **104**, 33-37.
4. B.-Y. Han, X.-X. Hu, J. Xu and G.-H. He, *Journal of Nanoscience and Nanotechnology*, 2018, **18**, 7933-7938.