Supporting Information

Reversible cobalt ion detection with imidazole-modified nanopipettes

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Chemicals and materials. Solutions were prepared using 18 MΩ·cm H_2O from a Milli-Q water purification system (Millipore Corp., Danvers, MA). Supporting electrolyte for current-voltage measurements consisted 0.1 M KCl (Mallinckrodt, Philipsburg, NJ) with 0.1 M phosphate buffer (J.T. Baker, Inc.). N-[3-(Triethoxysilyl)propyl]-4,5-dihydroimidazole (DHI, Gelest) was used for surface functionalization. Metal cation solutions were prepared from Cobalt (II) acetate tetrahydrate (J.T. Baker, Inc.). Potassium hydroxide (Mallinckrodt, Philipsburg, NJ) and hydrochloric acid (Mallinckrodt, Philipsburg, NJ) were used for adjusting the pH of electrolyte solution.

Nanopipette size characterization. Scanning electron micrographs (SEM) representative of typical nanopipettes used in this work are shown in Figure S1. From these images, the cone angle, determined from the 2 µm region of the nanopipette shank that extends from the tip (Figure S1b) can be measured, allowing the radius of the tip opening (r_{tip}Figure S1c) to be determined from the following equation:

$$R \approx \frac{2\gamma \cot\left(\frac{\theta}{2}\right)}{\pi\, r_{tip}} \qquad (1)$$

Here, R is the measured resistance of nanopipette, γ is specific resistance of the electrolyte employed and θ represents the cone angle of the nanopipette. A solution of 0.1 M KCl phosphate buffer with a specific conductivity of 30.2 mS/cm (pH 6.7) served as the electrolyte solution. Typical values measured for the resistance of nanopipette were on the order of 60 MΩ, determined from the I-V response over the range of -0.2 V to +0.2 V. Calculated tip diameters were typically on the order of 30 nm, in good agreement with the tip diameters observed by means of electron microscopy.

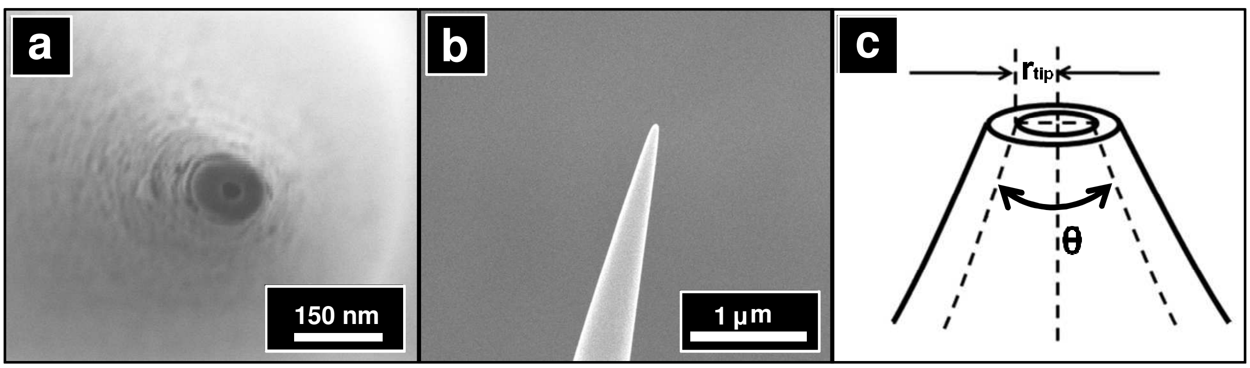


Figure S1. Scanning electron micrographs (SEM) of typically used nanopipettes in this experiment. (a) End-on image of nanopipette. Inner diameter is estimated to be 23 nm as viewed from the tip opening. (b) Side-on view of nanopipette. Cone angle over the first 2 µm is calculated to be 12º. (c) Schematic representation of nanopipette, r and θ represent tip radius and cone angle of nanopipette, respectively.

Response of non-modified nanopipettes to Co^{2+}: To show that this approach is valid for creation of Co^{2+}-sensing platform, it is mandatory to demonstrate that the changes in the rectified current are solely due to the formation of imidazole-Co^{2+} complexes, and not the physical adsorption of Co^{2+} to the nanopipette surface. Herein, we repeated the same experiments using non-modified nanopipettes to test their response to Co^{2+} under the same conditions. Figure S2 shows the variation of I-V plots after exposing the non-modified nanopipette to 50 µM and 100 µM Co^{2+}. Results showed that there is not any significant change in the I-V characteristics upon adding Co^{2+} into bulk electrolyte. These responses confirm the lack of ligand-target interaction, leaving the original nanopipette surface undisturbed. But after treatment of the nanopipette with DHI, binding of Co^{2+} takes place, yielding a nanopipette surface with net positive charges. It is worth mentioning that upon altering the pH to 2.6 changes the rectification ratio from 0.12 to 0.80. This effect is mainly due to the neutralization of silanol groups on the nanopipette wall in acidic environment that has been demonstrated previously.

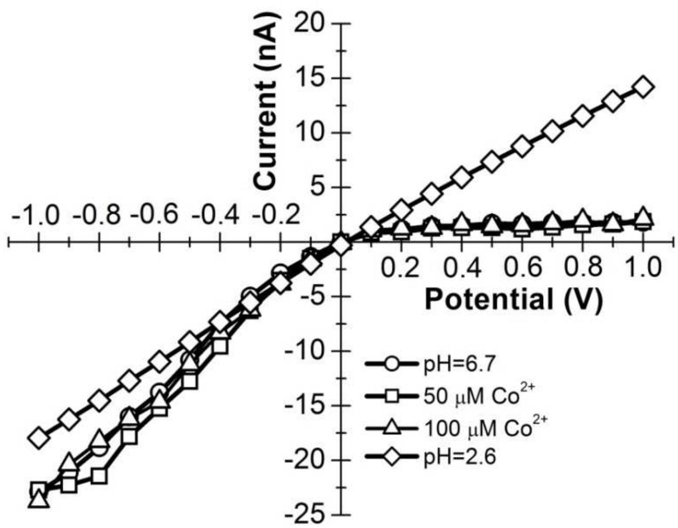
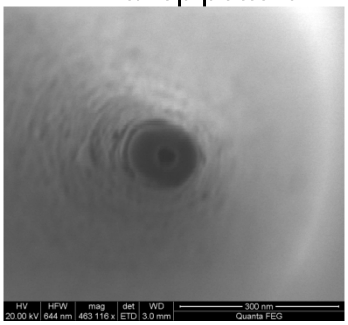


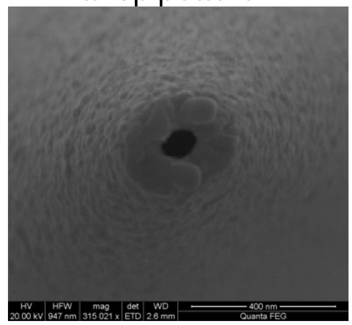
Figure S2. I-V response of non-modified nanopipettes with Co^{2+}. —○— represents I-V without Co^{2+} at pH=6.7; —□— stands for I-V response after addition of 50 µM Co^{2+} in the bath electrolyte; —△— stands for I-V response with 100 µM Co^{2+}; —◇— represents I-V response for pH altered to 2.6.

1. Nanopipette-01



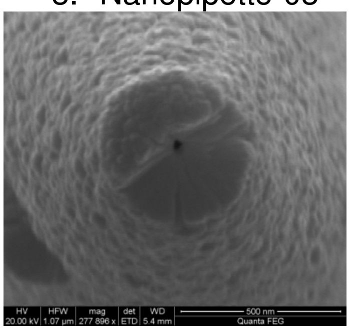
Scale: 480 pixel/300 nm
Inner diameter：36 pixel/23.0 nm

2. Nanopipette-02



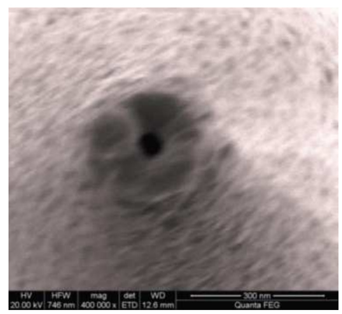
Scale: 430 pixel/400 nm
Inner diameter：65 pixel/60.0 nm

3. Nanopipette-03



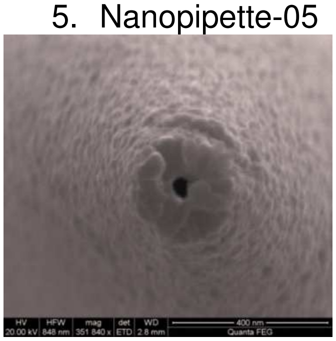
Scale: 478 pixel/500 nm
Inner diameter：21 pixel/22.0 nm

4. Nanopipette-04



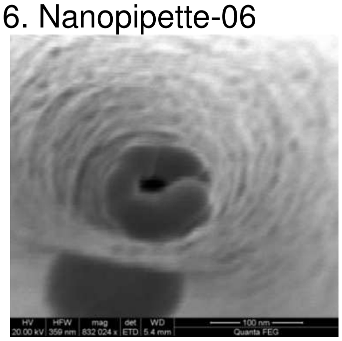
Scale: 420 pixel/300 nm
Inner diameter：55 pixel/39.0 nm

5. Nanopipette-05



Scale: 490 pixel/400 nm
Inner diameter：40 pixel/32.6 nm

6. Nanopipette-06



Scale: 290 pixel/100 nm
Inner diameter：70 pixel/24.1 nm

Figure S3. Scanning electron micrographs of end on view of six nanopipettes prepared using the same parameters employed in this study.