

Supplementary information for the paper:

**Ultrasensitive and Selective Detection of Alkali-Earth Metal Ions
Using Ion-Imprinted Au NPs Composites and Surface Plasmon
Resonance Spectroscopy**

Yaniv Ben-Amram, Ran Tel-Vered, Michael Riskin, Zhen-Gang Wang and Itamar Willner,*

To evaluate the morphology of the electropolymerized Au aggregated composite, the film was electropolymerized on one part of the electrode and was scanned at the boundary between the electropolymerized region and the bare electrode surface using AFM. Fig. S1 shows a typical image of the scanned region.

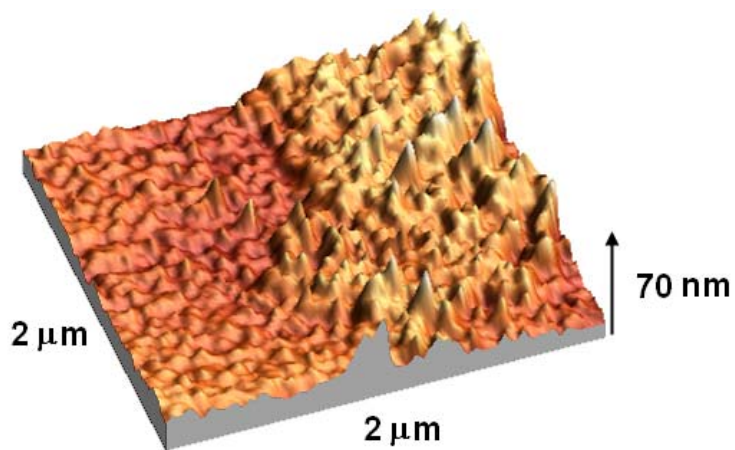


Fig. S1. An AFM image of the boundary region corresponding to the electropolymerized Au NPs composite on the bare Au electrode surface.

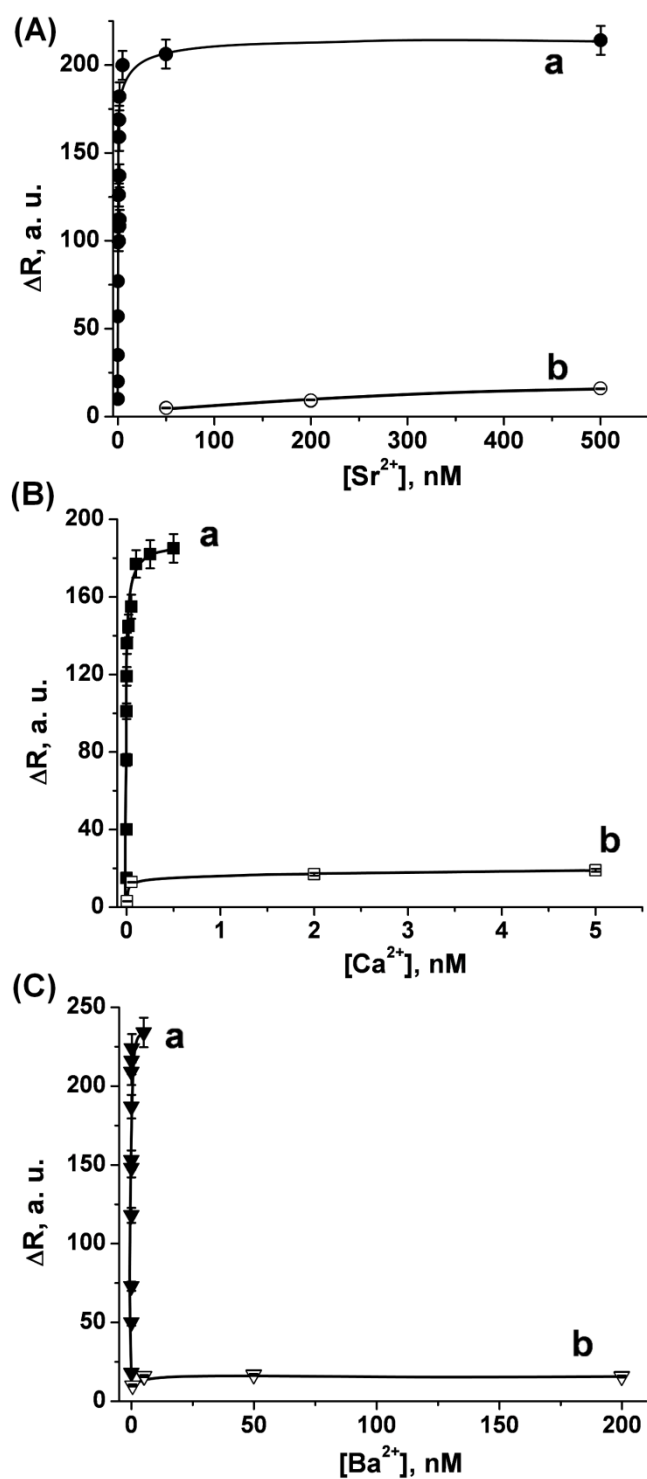


Fig. S2. Calibration curves relating the reflectance changes to the concentrations of: (A) Sr^{2+} on: (a) The Sr^{2+} -imprinted, and (b) The non-imprinted matrices, (B) Ca^{2+} on: (a) The Ca^{2+} -imprinted, and (b) The non-imprinted matrices, and (C) Ba^{2+} on: (a) The Ba^{2+} -imprinted, and (b) The non-imprinted matrices.

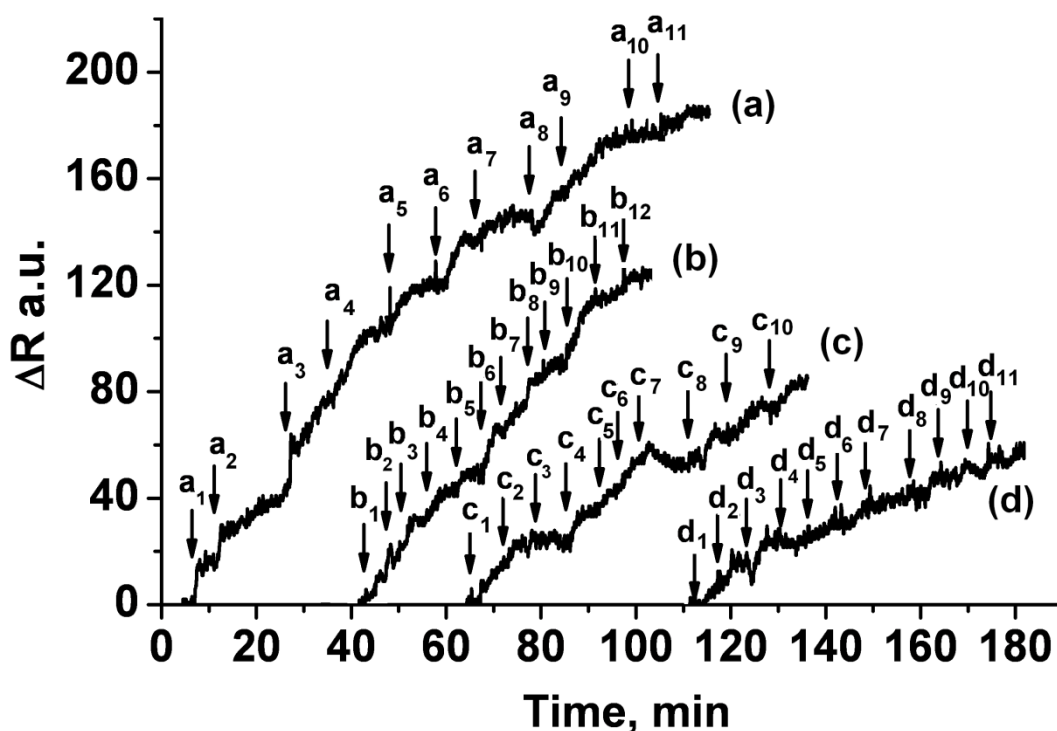


Fig. S3. Sensograms corresponding to the changes in the reflectance intensities of the Ca^{2+} -imprinted Au NPs matrix, at $\theta=63.5^\circ$, upon the addition of variable concentrations of: (a) Ca^{2+} : (a_1) 40, (a_2) 60, (a_3) 80, (a_4) 100 fM, and (a_5) 2, (a_6) 5, (a_7) 20, (a_8) 50, (a_9) 100, (a_{10}) 250, and (a_{11}) 500 pM. (b) Mg^{2+} : (b_1) 40, (b_2) 60, (b_3) 80, (b_4) 100 fM, and (b_5) 2, (b_6) 5, (b_7) 20, (b_8) 50, (b_9) 100, (b_{10}) 250 pM, and (b_{11}) 1, and (b_{12}) 5 nM. (c) Ba^{2+} : (c_1) 5, (c_2) 20, (c_3) 50, (c_4) 100, (c_5) 250, (c_6) 500 pM, and (c_7) 1, (c_8) 5, (c_9) 50, and (c_{10}) 200 nM. (d) Sr^{2+} : (d_1) 5, (d_2) 20, (d_3) 50, (d_4) 100, (d_5) 250, (d_6) 500 pM, and (d_7) 1, (d_8) 5, (d_9) 50, (d_{10}) 200, and (d_{11}) 500 nM.

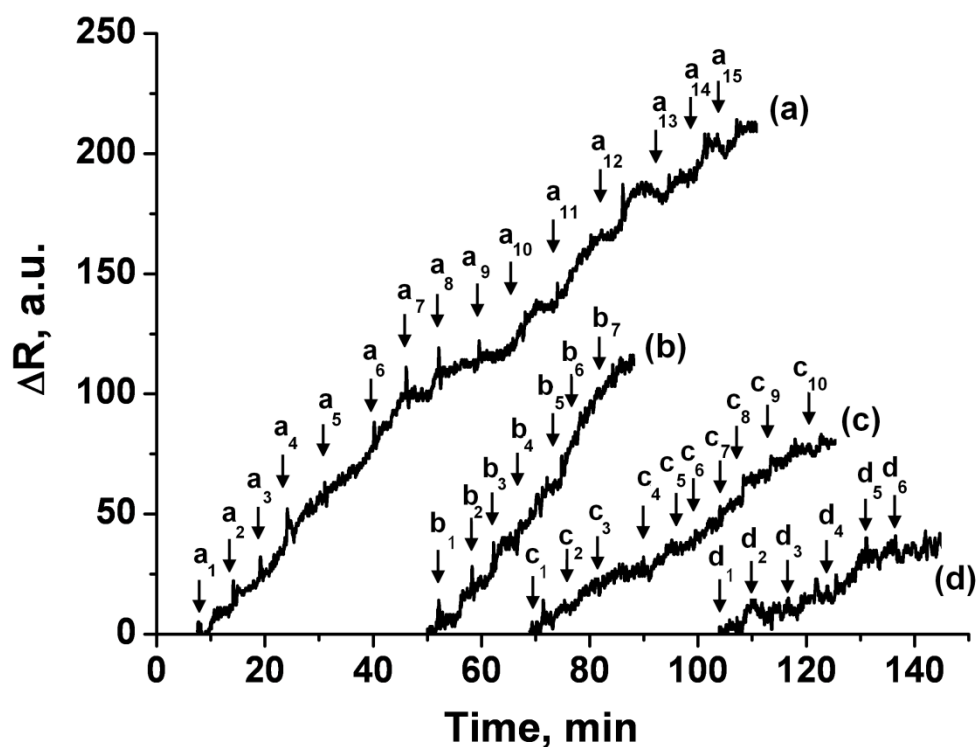


Fig. S4. Sensograms corresponding to the changes in the reflectance intensities of Sr^{2+} -imprinted Au NPs matrix, at $\theta=63.5^\circ$, upon the addition of variable concentrations of: **(a)** Sr^{2+} : (a_1) 20, (a_2) 40, (a_3) 60, (a_4) 80, (a_5) 100 fM, and (a_6) 2, (a_7) 5, (a_8) 20, (a_9) 50, (a_{10}) 100, (a_{11}) 250, (a_{12}) 500 pM, and (a_{13}) 1, (a_{14}) 5, and (a_{15}) 50 nM. **(b)** Ca^{2+} : (b_1) 20, (b_2) 50, (b_3) 100, (b_4) 250, (b_5) 500 pM, and (b_6) 1, and (b_7) 5 nM. **(c)** Mg^{2+} : (c_1) 100 fM, and (c_2) 2, (c_3) 5, (c_4) 20, (c_5) 50, (c_6) 250, (c_7) 500 pM, and (c_8) 1, (c_9) 5, and (c_{10}) 50 nM. **(d)** Ba^{2+} : (d_1) 20, (d_2) 50, (d_3) 100, (d_4) 250, (d_5) 500 pM, and (d_6) 1 nM.

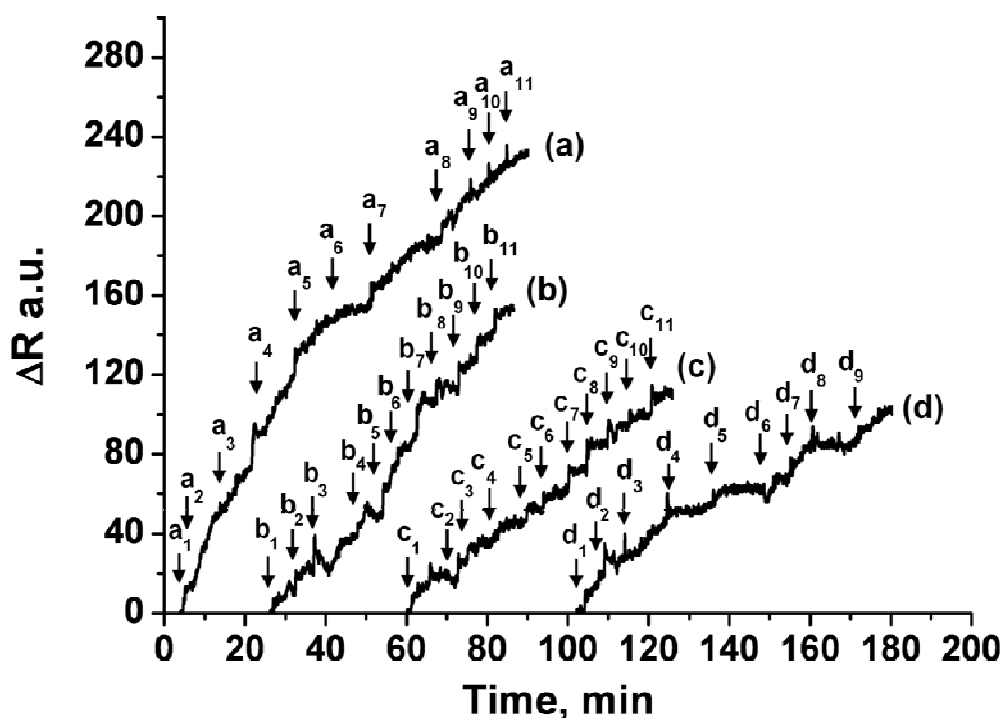


Fig. S5. (a) Sensograms corresponding to the changes in the reflectance intensities of Ba²⁺-imprinted Au NPs matrix, at $\theta=63.5^\circ$, upon the addition of variable concentrations of: (a) Ba²⁺: (a₁) 1, (a₂) 5, (a₃) 10, (a₄) 20, (a₅) 40, (a₆) 60, (a₇) 80, (a₈) 100 fM, and (a₉) 2, (a₁₀) 5, and (a₁₁) 20 pM. (b) Ca²⁺: (b₁) 100 fM, and (b₂) 2, (b₃) 5, (b₄) 20, (b₅) 50, (b₆) 100, (b₇) 250 pM, and (b₈) 1, (b₉) 5, (b₁₀) 50, and (b₁₁) 200 nM. (c) Mg²⁺: (c₁) 100 fM, and (c₂) 2, (c₃) 5, (c₄) 20, (c₅) 50, (c₆) 100 (c₇) 250, (c₈) 500 pM, and (c₉) 1, (c₁₀) 5, and (c₁₁) 50 nM. (d) Sr²⁺: (d₁) 60, (d₂) 80, (d₃) 100 fM, and (d₄) 2, (d₅) 5, (d₆) 20, (d₇) 50, (d₈) 100, and (d₉) 250 pM.

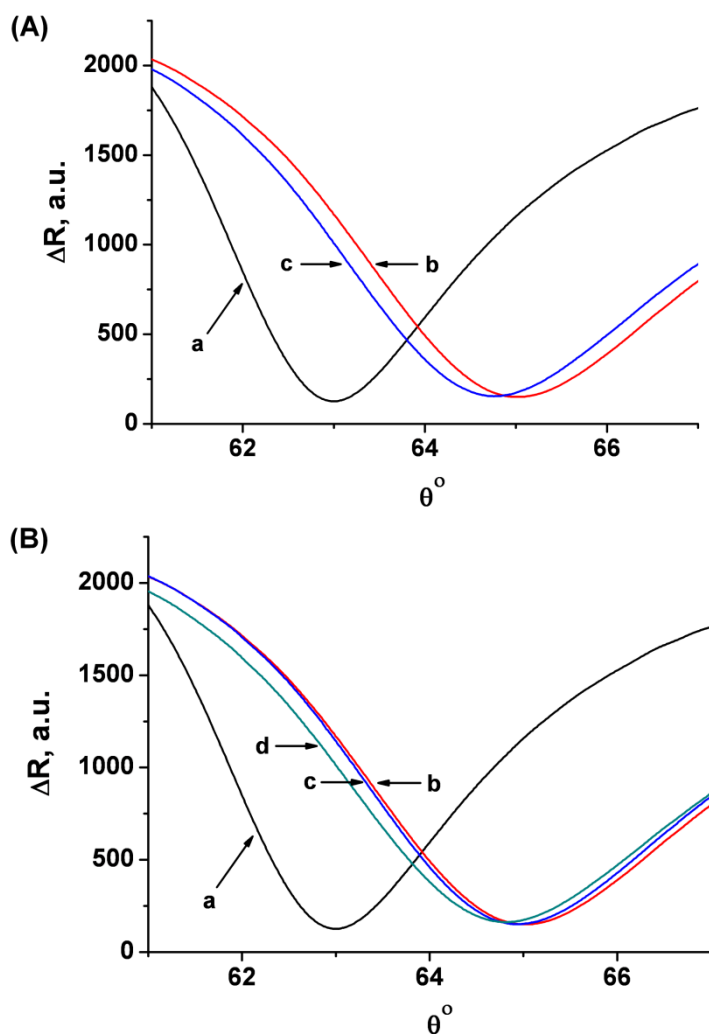


Fig. S6. (A) SPR curves corresponding to: (a) The thioaniline-modified Au surface before electropolymerization. (b) The bis-aniline-crosslinked Au NPs composite electropolymerized on the Au surface in the presence of Ba^{2+} , 10 mM. (c) The Ba^{2+} -imprinted bis-aniline-crosslinked Au NPs matrix, following the treatment of the matrix with HCl, 0.03 M, for 5 minutes. (B) SPR curves corresponding to: (a) The thioaniline-modified Au surface before electropolymerization. (b) The bis-aniline-crosslinked Au NPs composite electropolymerized on the Au surface in the presence of Ba^{2+} , 10 mM. (c) The Ba^{2+} -imprinted bis-aniline-crosslinked Au NPs matrix, following the treatment of the matrix with water, for 10 minutes. (d) The Ba^{2+} -imprinted bis-aniline-crosslinked Au NPs matrix, following the treatment of the matrix with water, for 5 hours.