

## Electrochemically Programmed Chemodosimeter on Ultrathin Platinum Films

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## Reagents and instrumentation

Hexaammineruthenium(II) chloride, Hexaammineruthenium(III) chloride, Potassium hydroxide, and sodium hydroxide were purchased from Sigma-Aldrich and were used as received. 6-Ferrocenyl-1-hexanethiol (FcSH) was procured from Dojindo Laboratories. Thiol-functionalized rhodamine chemodosimeter (**RhSH**) was synthesized using procedures previously reported from our groups.<sup>1</sup> All other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared using deionized water (> 18 M $\Omega$  cm resistivity) purified in a Milli-Q system.

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) were performed with a CHI 660 electrochemical workstation (CH instruments, Austin, TX). Electrochemical experiments were performed using a two-compartment three-electrode cell. Platinum electrode (1.6 mm diameter, Bioanalytical Systems, Inc.) and platinum-minigrad working electrode (ALS Co., Japan) as working electrodes, Ag/AgCl (Bioanalytical Systems, Inc.) as reference electrode, and platinum wire as counter electrode were employed. The width of grid line and space between lines of Pt-minigrad working electrode are 150  $\mu$ m and 100  $\mu$ m, respectively. Fluorescence image were taken with a confocal laser scanning microscope (LSM 510, Carl Zeiss). The HeNe-laser (543 nm, 0.5 mW) was used.

## Experimental procedures

### 1) Preparation of FcSH-modified electrode

Platinum electrode was polished 0.3  $\mu\text{m}$  alumina powder (Buehler, Lake Bluff, MN) and rinsed with deionized water. Then, the electrode was immersed in a chloroform solution containing 1 mM FcSH for 12 h. After the electrodes were removed from the solution, it was thoroughly rinsed with acetone and chloroform to remove excess FcSH and dried by nitrogen blow. Electrochemical reductive desorption of FcSH-SAMs was performed by applying -1.2 V to the electrode for 2 min in 0.5 M KOH ethanolic solution. 0.1 M KCl solution was utilized as electrolyte for CV experiments.

### 2) Preparation of **RhSH**-modified electrode and electrochemical experiments

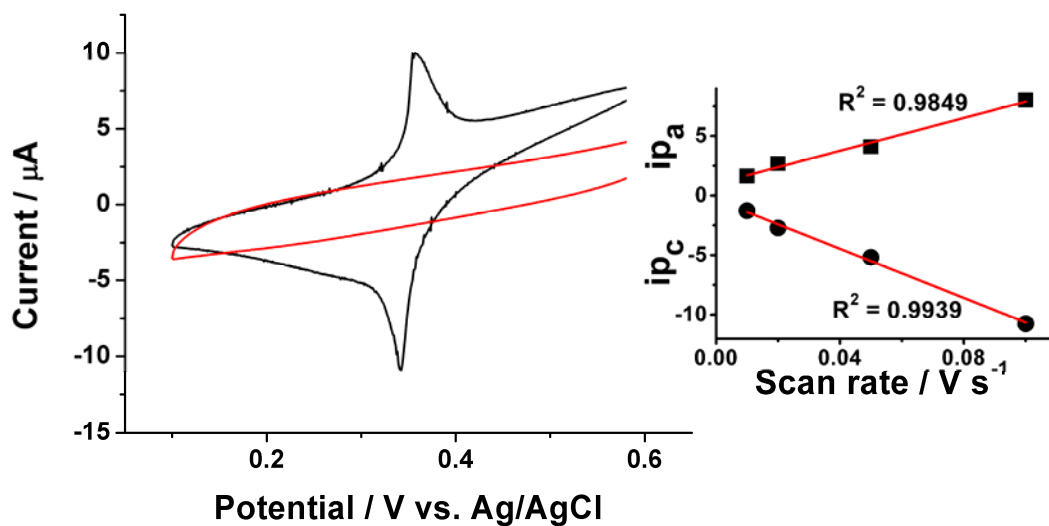
Platinum electrode was polished 0.3  $\mu\text{m}$  alumina powder (Buehler, Lake Bluff, MN) and rinsed with deionized water. Platinum-minigrid working electrode was cleaned using oxygen plasma in a conventional asher (Plasma finish V15-G, power: 100 W, O<sub>2</sub> gas flow: 300 sccm, time: 10 min). Platinum-minigrid working electrode was immersed in an ethanolic solution containing 1% (v/v) aminopropyltrimethoxysilane for 2 h to prevent the non-specific adsorption of **RhSH**. Then, **RhSH** self-assembled monolayers (SAMs) were formed by immersing platinum and platinum-minigrid working electrodes in 5 mM **RhSH** methanolic solution for 18 h. After the electrodes were removed from the solution, they were thoroughly rinsed with acetone and methanol to remove excess **RhSH** and dried by nitrogen blow.

The ring-opening of **RhSH**-SAMs was conducted in 0.01 M Cu<sup>2+</sup> methanolic solution for 1 h. Cu<sup>2+</sup> removal for the ring-closing was performed in 0.5 M NaOH solution for 1 h. Electrochemical reductive desorption of **RhSH**-SAMs was performed by applying -1.2 V to the electrode for 2 min in 0.5 M KOH ethanolic solution. Before electrochemical measurements, platinum and platinum-minigrid working electrodes were thoroughly rinsed with methanol and water and dried by nitrogen blow. 5 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup> in 0.1 M KCl was utilized for CV and EIS experiments. KOH and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup> solutions were thoroughly deaerated with highly pure nitrogen before experiments. The impedance data were obtained at

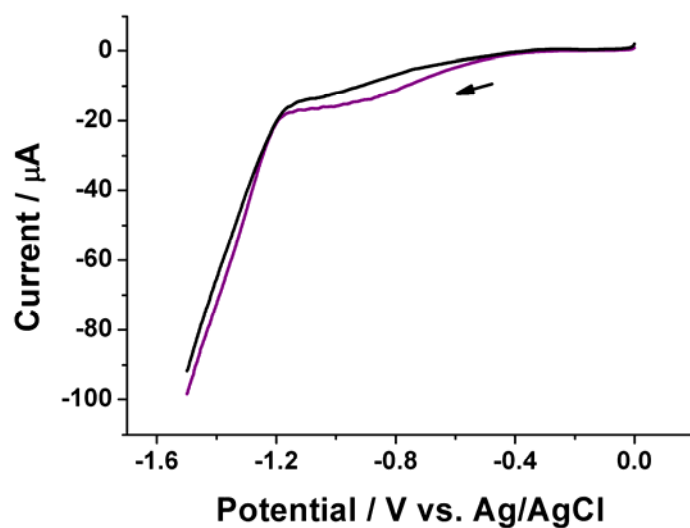
the equilibrium potential of  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  and fitted to an appropriate equivalent circuit using ZsimpWin 3.0 software (Echem Software). The frequency range is from 0.5 Hz to 100 kHz. The ac amplitude of 5 mV was applied.

### Reference

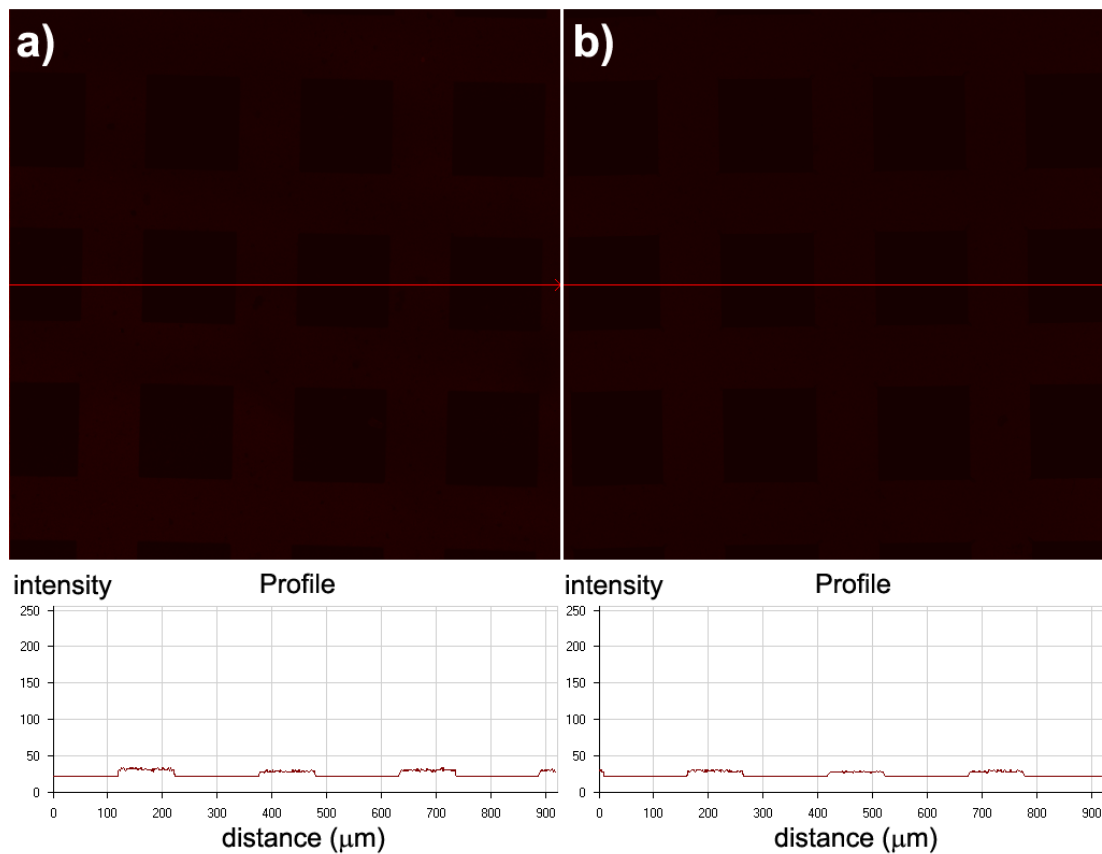
1. Y.-R. Kim, H. J. Kim, J. S. Kim and H. Kim, *Adv. Mater.*, 2008, **20**, 4428.



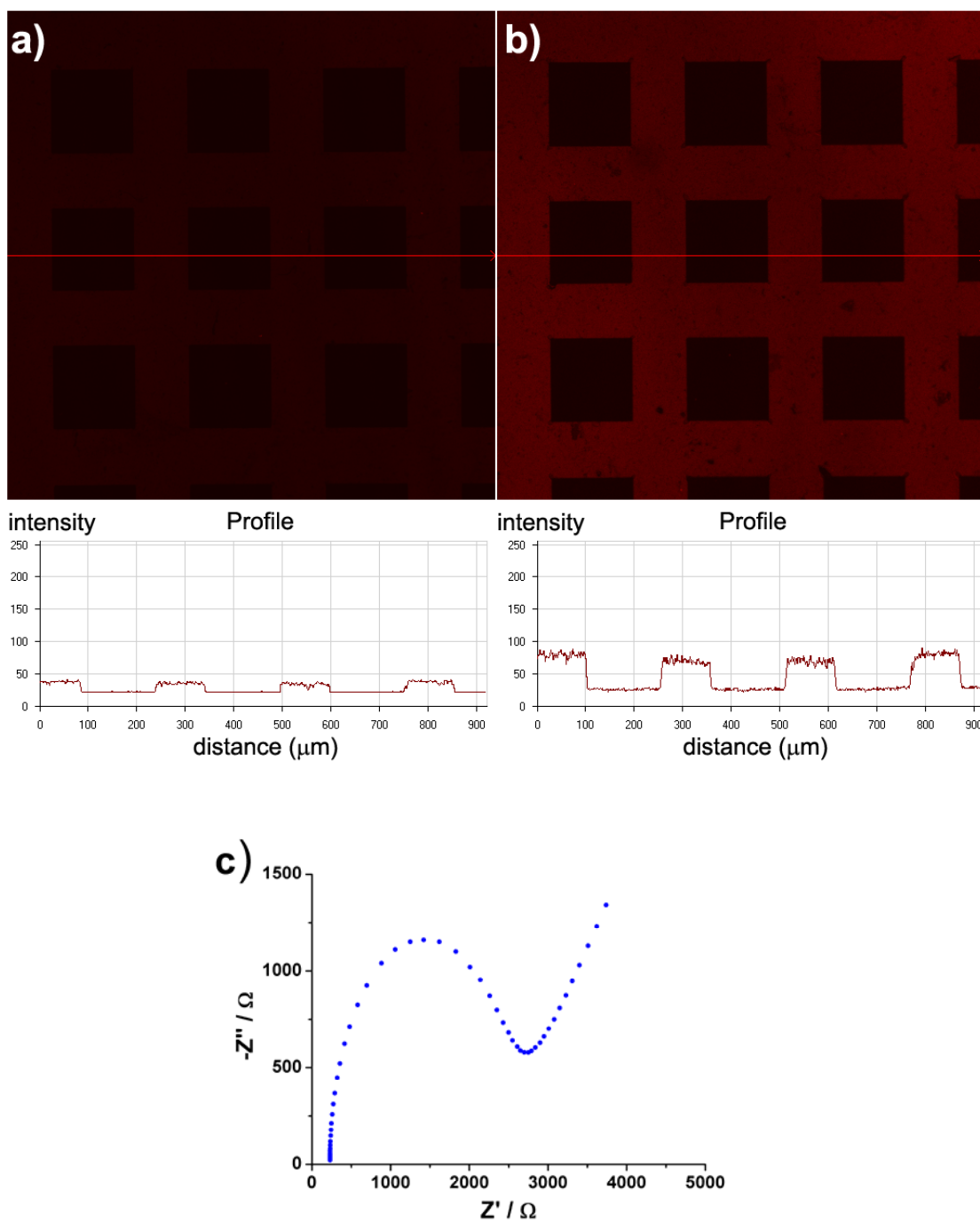
**Fig. S1** CV curves of FcSH-modified (black) and FcSH-desorbed (red) platinum electrodes in 0.1 M KCl. The scan rate was 100 mV/s. Inset indicates anodic and cathodic peak currents at different scan rates.



**Fig. S2** LSVs on platinum electrodes with (purple) or without (black) **RhSH-SAMs** in 0.5 M ethanolic KOH solution. The scan rate was 100 mV/s. The arrow indicates that the potential was scanned in the negative direction.

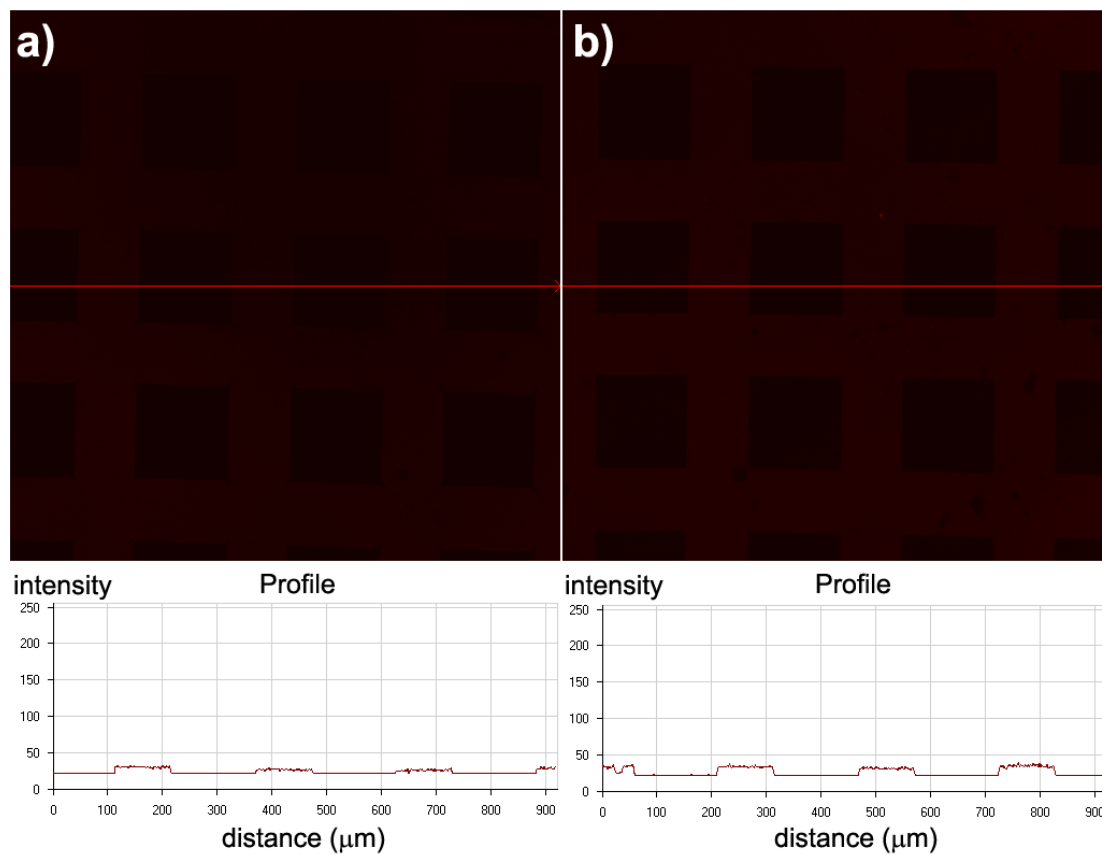


**Fig. S3** Fluorescence images on bare (a) and **RhSH**-modified (b) platinum electrodes.

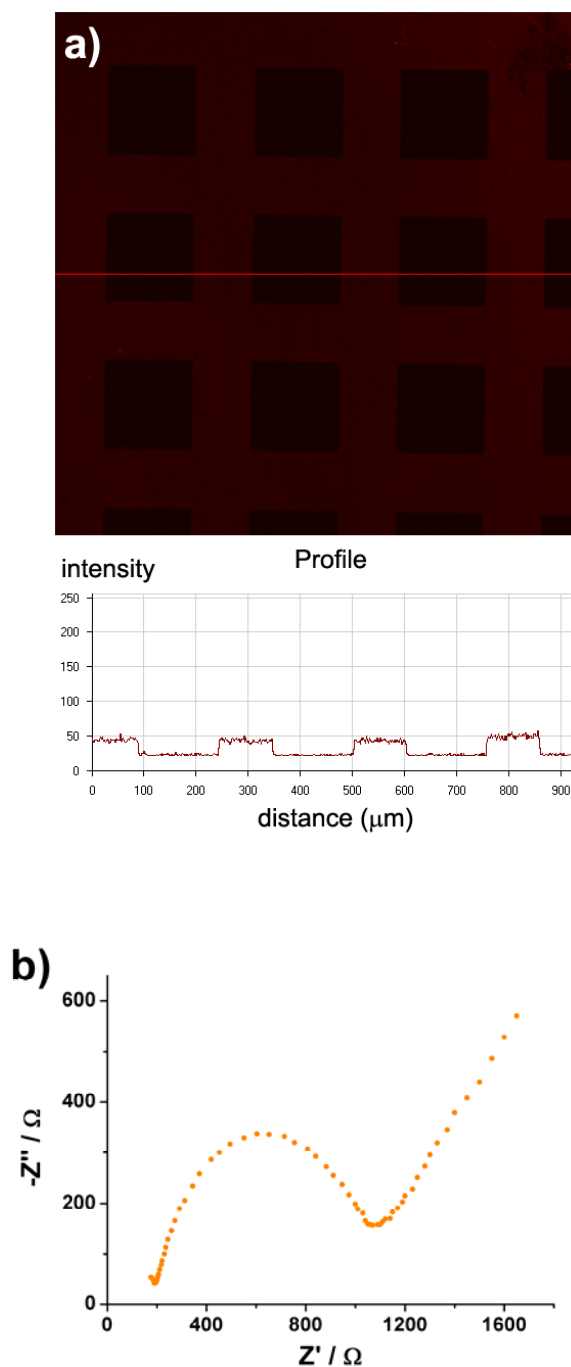


**Fig. S4** Fluorescence images on Cu<sup>2+</sup>-extracted **RhSH**-modified platinum electrode by NaOH solution (a) and **RhSH**-modified platinum electrode after Cu<sup>2+</sup>-induced ring-reopening (b). Nyquist plot on ring-reopened **RhSH**-modified platinum electrode (c).





**Fig. S5** Fluorescence images on **RhSH-SAMs** desorbed platinum electrodes before (a) and after (b) the immersion in 0.01 M Cu<sup>2+</sup> methanolic solution for 1 h.



**Fig. S6** Fluorescence images (a) and Nyquist plot (b) on **RhSH**-modified platinum electrodes after the immersion in methanolic solution containing the mixtures of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  at a concentration of 0.1 M for 1 h.