Supplementary Online Material

Printable non-enzymatic glucose biosensors using carbon nanotube-PtNPs nanocomposite modified with AuRu for improved selectivity

Tran N. H. Nguyen[a], Xin Jin[b], James K. Nolan[a], Jian Xu[a], Khanh Vy H. Le[a], Stephanie Lam[a], Yi Wang[a], Muhammad A. Alam[b], Hyowon Lee[a]

[a]Weldon School of Biomedical Engineering, Birck Nanotechnology Center, Center for Implantable Device, [b]School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN 47907 USA

Number of pages: 9

Number of figures: 7

Number of tables: 4

* Corresponding author: hwlee@purdue.edu

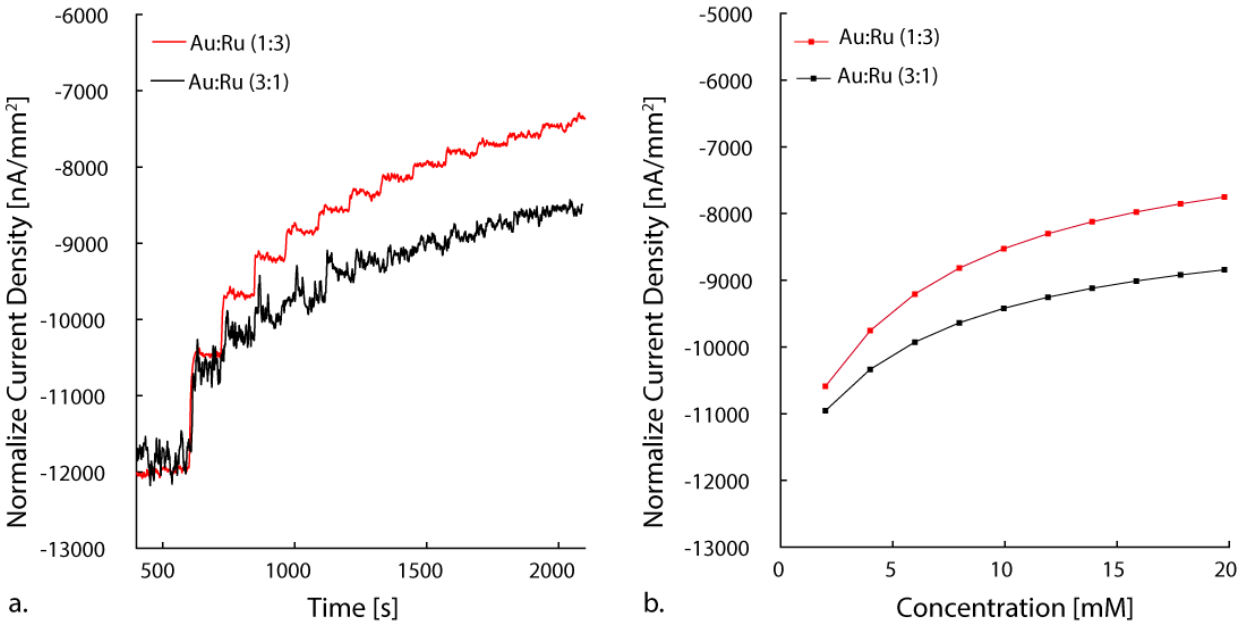

Figure S1. (a). Current-time curve obtained at Au-RuNPs biosensor with two different electrodepositing concentration of gold(III) chloride hydrate (HAuCl4) and ruthenium(III) chloride hydrate ($RuCl_3$) with successive addition of glucose with every 2 mM increment in 0.01 M PBS (pH 7.4) at -0.1 V. (b). Non-linear feature of the steady-state response for glucose at Au-RuNPs biosensor with two different electrodepositing concentration of $HAuCl_4$ to $RuCl_3$ in 0.01 M PBS (pH 7.4) at - 0.1 V.

	Au:Ru (1:3)	Au:Ru (3:1)
N_0 (mol/m^2)	2.49E-05	1.85E-05
k_F (m^3/s/mol)	0.0867	0.0862
k_R (1/s)	0.455	0.455
k'_R (1/s)	0.044	0.044

Table S1. Key fitting parameters in the simulation for experiment with two different electrodepositing concentrations of $HAuCl_4$ and $RuCl_3$.

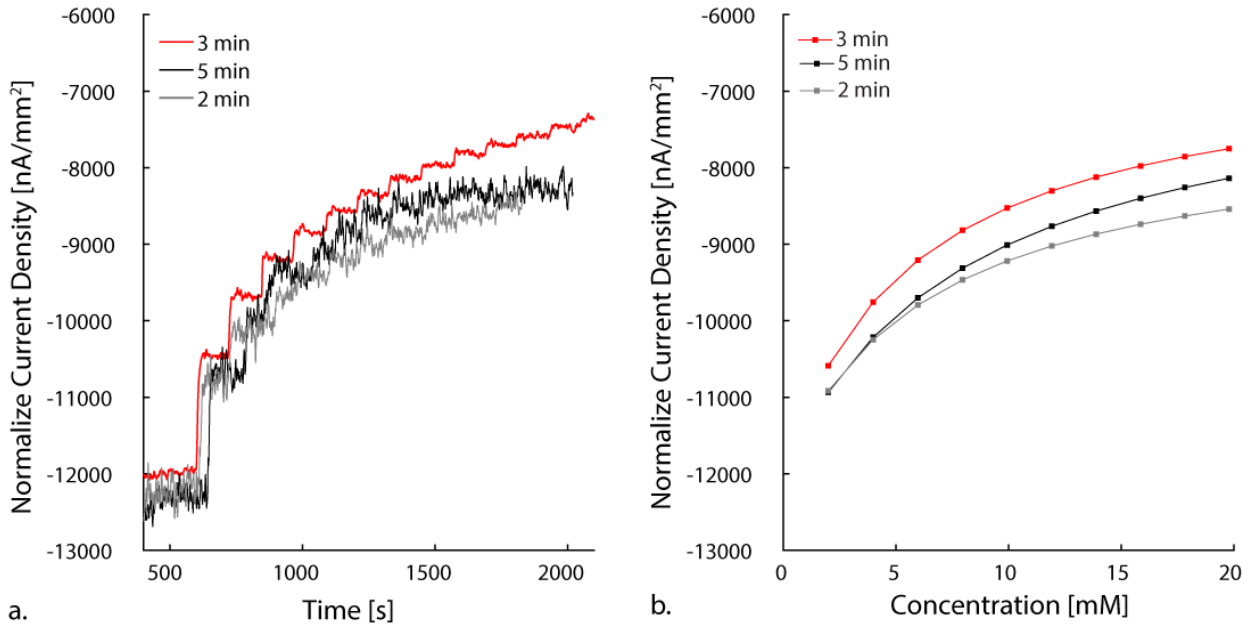

Figure S2. (a). Current-time curve obtained at Au-RuNPs biosensor with different electrodepositing time using 1:3 ratio of $HAuCl_4$ to $RuCl_3$ solution with successive addition of glucose with every 2 mM increment in 0.01 M PBS (pH 7.4) at -0.1 V. (b). Non-linear feature of the steady-state response for glucose at Au-RuNPs biosensor with different electrodepositing time using 1:3 ratio of $HAuCl_4$ to $RuCl_3$ solution in 0.01 M PBS (pH 7.4) at -0.1 V.

	Au:Ru (1:3) - 2 min	Au:Ru (1:3) - 3 min	Au:Ru (1:3) - 5 min
N_0 (mol/m^2)	2.08E-05	2.49E-05	2.48E-05
k_F (m^3/s/mol)	0.0774	0.0867	0.0605
k_R (1/s)	0.455	0.455	0.455
k'_R (1/s)	0.044	0.044	0.044

Table S2. Key fitting parameters in the simulation for experiment with different electrodepositing time using 1:3 ratio of $HAuCl_4$ to $RuCl_3$ solution.

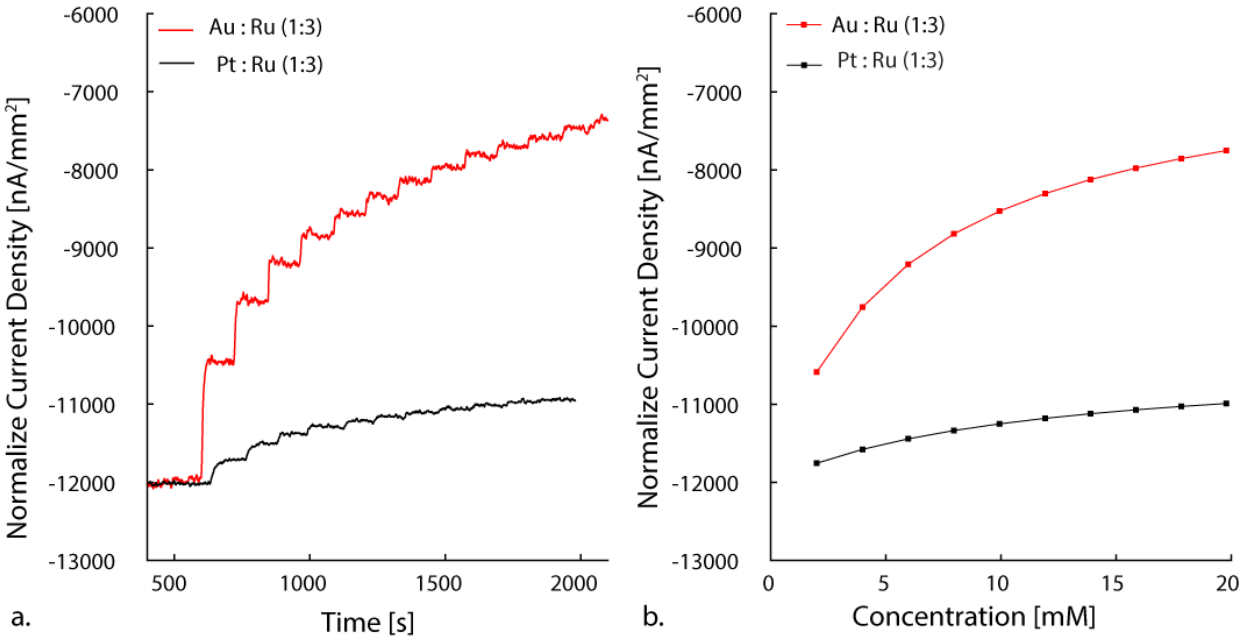

Figure S3. (a). Current-time curve obtained at Au-RuNPs biosensor with two different bimetallic systems, Au:Ru (1:3) and Pt:Ru (1:3), with successive addition of glucose with every 2 mM increment in 0.01 M PBS (pH 7.4) at -0.1 V. (b). Non-linear feature of the steady-state response for glucose at two different bimetallic systems, Au:Ru (1:3) and Pt:Ru (1:3) in 0.01 M PBS (pH 7.4) at -0.1 V.

	Au:Ru (1:3)	Pt: Ru (3:1)
N_0 (mol/m^2)	2.49E-05	7.05E-06
k_F (m^3/s/mol)	0.0867	0.0467
k_R (1/s)	0.455	0.455
k'_R (1/s)	0.044	0.044

Table S3. Key fitting parameters in the simulation for experiment with two different bimetallic systems, Au:Ru (1:3) and Pt:Ru (1:3).

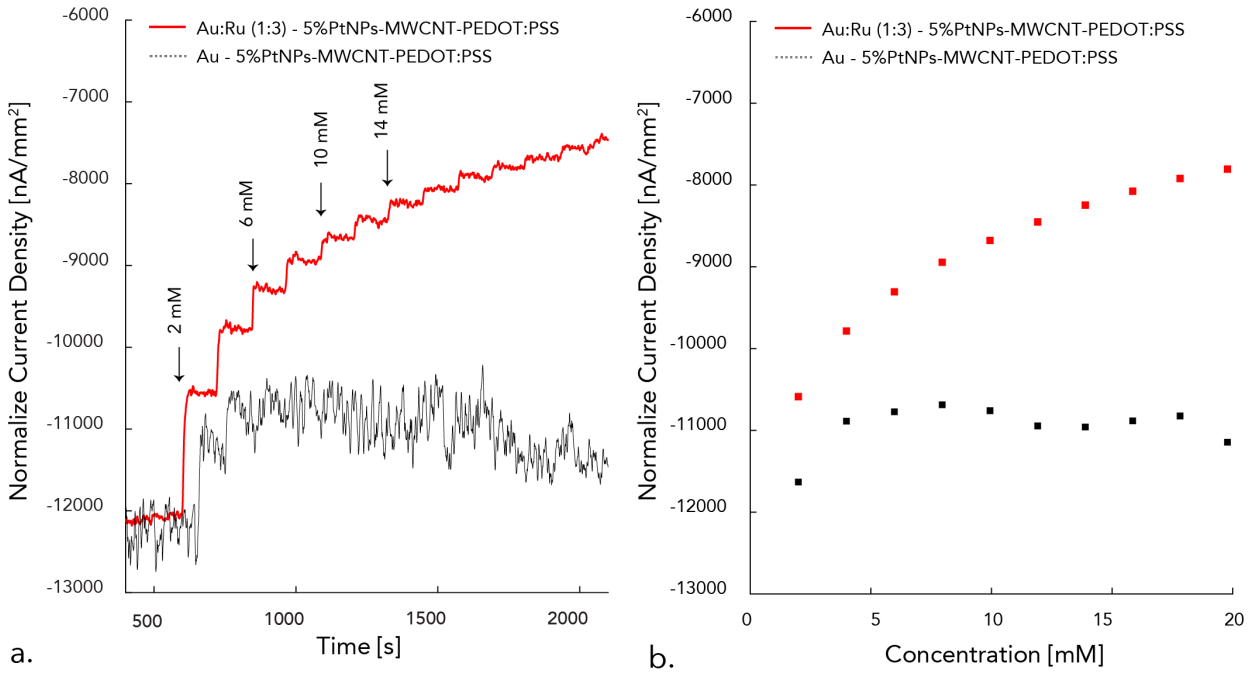

Figure S4. (a). Current-time curve obtained at Au-RuNPs nanocomposite biosensor and Au nanocomposite biosensor with successive addition of glucose with every 2 mM increment in 0.01 M PBS (pH 7.4) at -0.1 V vs. Ag/AgCl. (b). Non-linear feature of the steady-state response for glucose at Au-RuNPs biosensor and Au nanocomposite biosensor in 0.01 M PBS (pH 7.4) at - 0.1 V vs. Ag/AgCl.

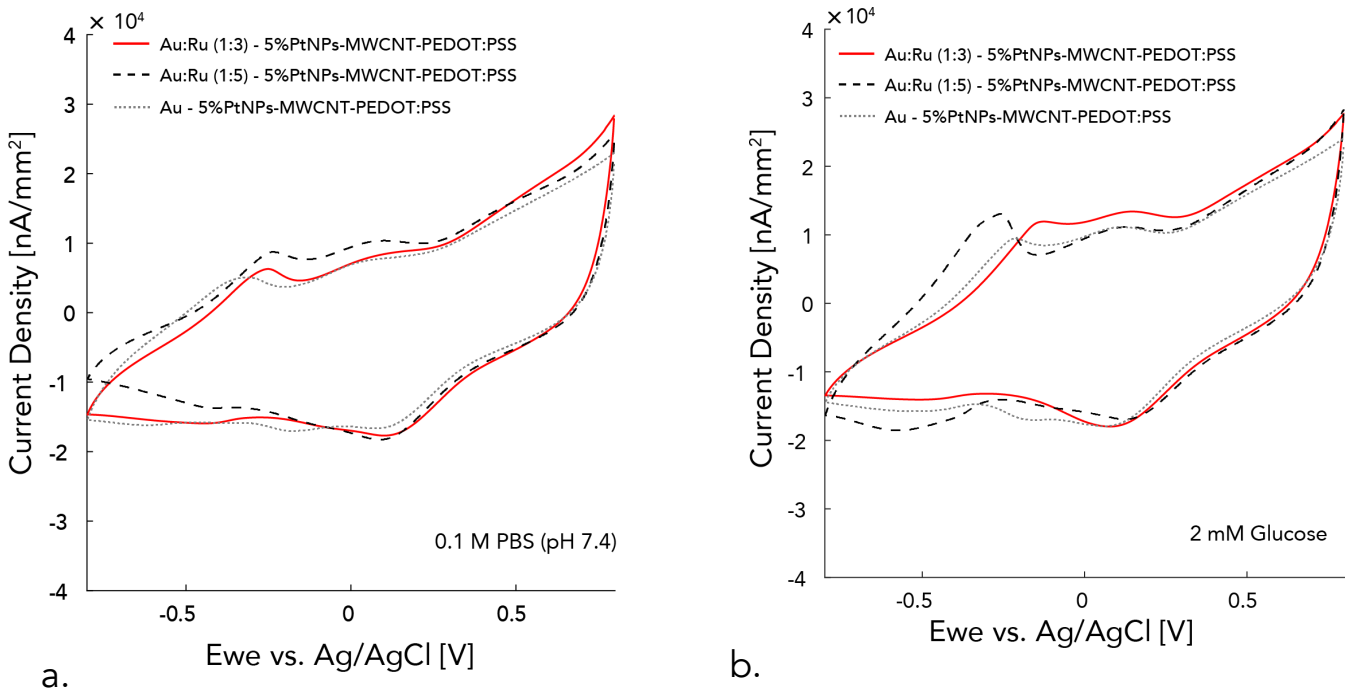

Figure S5. (a) Cyclic voltammetry of the Au-RuNPs (1:3)-nanocomposite, Au-RuNPs (1:5)-nanocomposite and Au-nanocomposite biosensors in 0.01 M PBS (pH 7.4). Scan rate = 20 mV/s. (b). Cyclic voltammetry of the Au-RuNPs (1:3)-nanocomposite, Au-RuNPs (1:5)-nanocomposite and Au-nanocomposite biosensors in 2 mM glucose. Scan rate = 20 mV/s.

Au-RuNPs (1:5) electrode showed the highest currently density compared to the other electrodes in PBS solution. However, in glucose-spiked samples, the anodic peak at -0.1 V, which is considered to be related to the direct electrooxidation of glucose, was the highest for Au-RuNPs (1:3). Thus, we used this composition as our electrode material to fabricate our non-enzymatic glucose biosensor.

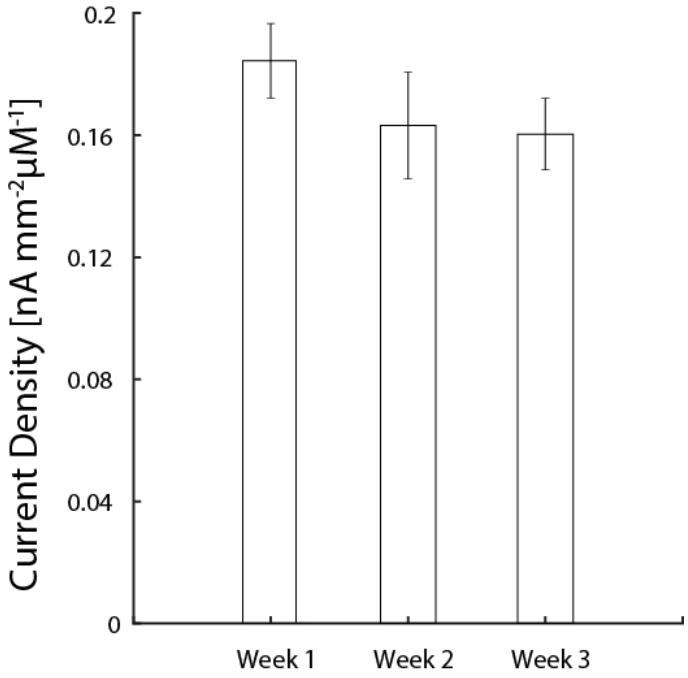

Figure S6. Biosensor lifetime measurement where the glucose sensitivity for Au-RuNPs biosensors were monitored over a period of 3 weeks (n=4). The sensors were stored in an oven at 37 °C when they were not in use.

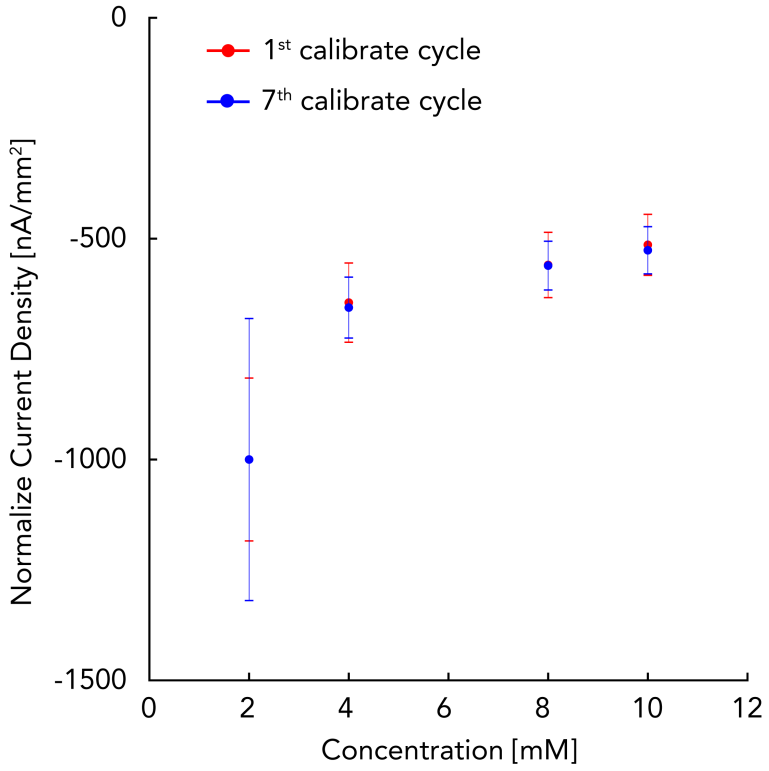

Figure S7. Non-linear feature of the steady-state response for glucose with Au-RuNPs-nanocomposite biosensor to different glucose concentration at detection potential of -0.1 V vs. Ag/AgCl through continuous calibration cycles. The sensor was washed with DI water between calibrations and cleaned electrochemically with 5 cyclic voltammetries between 0 and 1.5 V in 0.5 M H_2SO_4. Scan rate = 100 mV s^{-1}.[1,2]

Type of electrode	Fabrication method	Estimated cost
Au-RuNPs-PtNPs nanocomposite	Direct ink writing/Electrodeposition	$0.83/device

a.

Chemical	Size (mg)	Cost ($)	Amount need for 1 batch (mg)	Cost for 1 batch ($)	Total cost for 1 batch	Cost for each device ($)
HAuCl4	1000	114.3	42	4.80	166.42	0.83
RuCl3	1000	43.2	77	3.33		
PtNPs	250	283.5	126.58	143.54		
MWCNT	1000	17	25	0.43		
PEDOT:PSS	25000	179.1	2000	14.33		

b.

Table S4. a. Estimate fabrication cost for one Au-RuNPs-nanocomposite non-enzymatic biosensor. b. Break down fabrication cost for each ink batch.

We was able to cut the cost due to printing process and the size of our electrode. We can print at least 100 to 200 electrodes for each ink batch. Even though the surfaces were coating with Au and RuNPs, they were derived from electrodepostion of $HAuCl_4$ and $RuCl_3$ solution, which were only required 2.5 mM and 7.5 mM per batch.

Reference

1. Lee, W. C. *et al.* Comparison of enzymatic and non-enzymatic glucose sensors based on hierarchical Au-Ni alloy with conductive polymer. *Biosens. Bioelectron.* **130**, 48–54 (2019).
2. Márquez, A., Jiménez-Jorquera, C., Domínguez, C. & Muñoz-Berbel, X. Electrodepositable alginate membranes for enzymatic sensors: An amperometric glucose biosensor for whole blood analysis. *Biosens. Bioelectron.* **97**, 136–142 (2017).