Electronic Supplementary Material (ESI) for Faraday Discussions.

Enzyme-modified Pt nanoelectrodes for glutamate detection

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Figure S1. Michaelis-Menten parameters calculation based on data in Figure 4, where $1/i$ was plotted as the y-axis and $1/c$ was plotted as the x-axis.

Figure S2. Cyclic voltammograms of blank and glutamate on glutamate oxidase-modified Pt nanoelectrodes with three repeated runs overlapped.

Figure S3. Box plot and two-sample t-test for current at +0.7 V vs Ag/AgCl/1 M KCl for blank and different glutamate concentrations.

Figure S4. Relationship between glutamate concentration and current for the second GluOx-modified Pt nanoelectrode corresponding to Figures 8A and 8B in manuscript.

Figure S5. Relationship between glutamate concentration and current for the third GluOx-modified Pt nanoelectrode corresponding to Figures 8C and 8D in manuscript.

Figure S6. Michaelis-Menten parameters calculation for carbon fiber microelectrode.

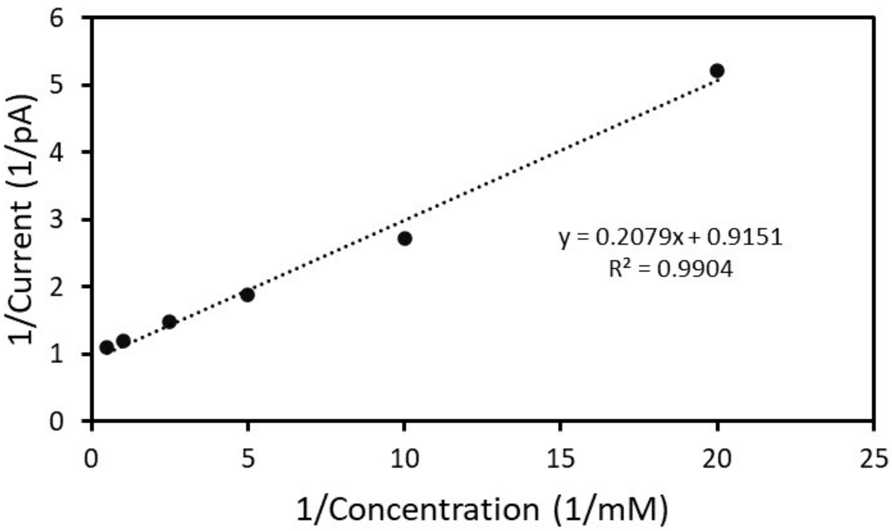

Figure S1. Michaelis-Menten parameters calculation based on data in Figure 4, where $1/i$ was plotted as the y-axis and $1/c$ was plotted as the x-axis. Black solid circle is the experimental data and dashed line is the best linear regression line. The intercept of the best linear regression line is $1/i_{max}$ and the slope is $K_m/i_{max.}$ Based on the intercept and slope, i_{max} was calculated to be 1.093 pA and K_m was calculated to be 0.227 mM.

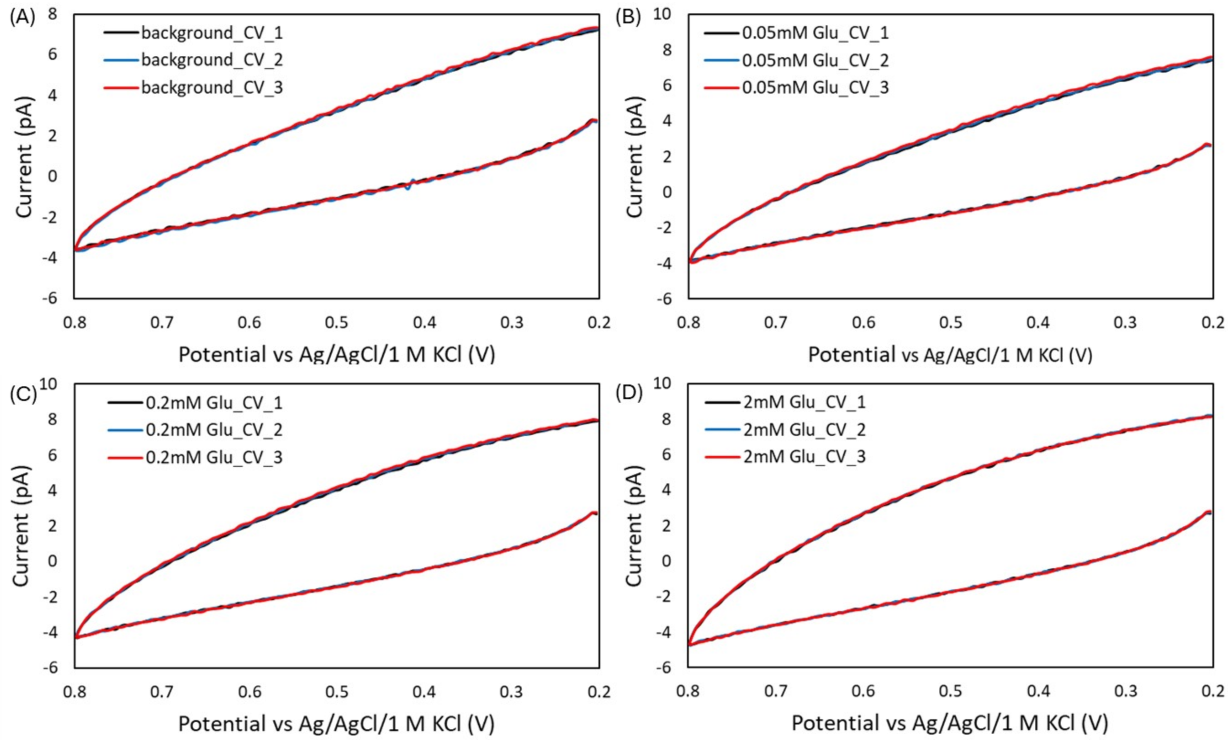

Figure S2. Cyclic voltammograms of blank and glutamate on glutamate oxidase-modified Pt nanoelectrodes with three repeated runs overlapped. (A) background solution, (B) 0.05 mM glutamate solution, (C) 0.2 mM glutamate solution, and (D) 2 mM glutamate solution. The three repeated CVs measured in blank and each glutamate solution with different concentrations overlapped well.

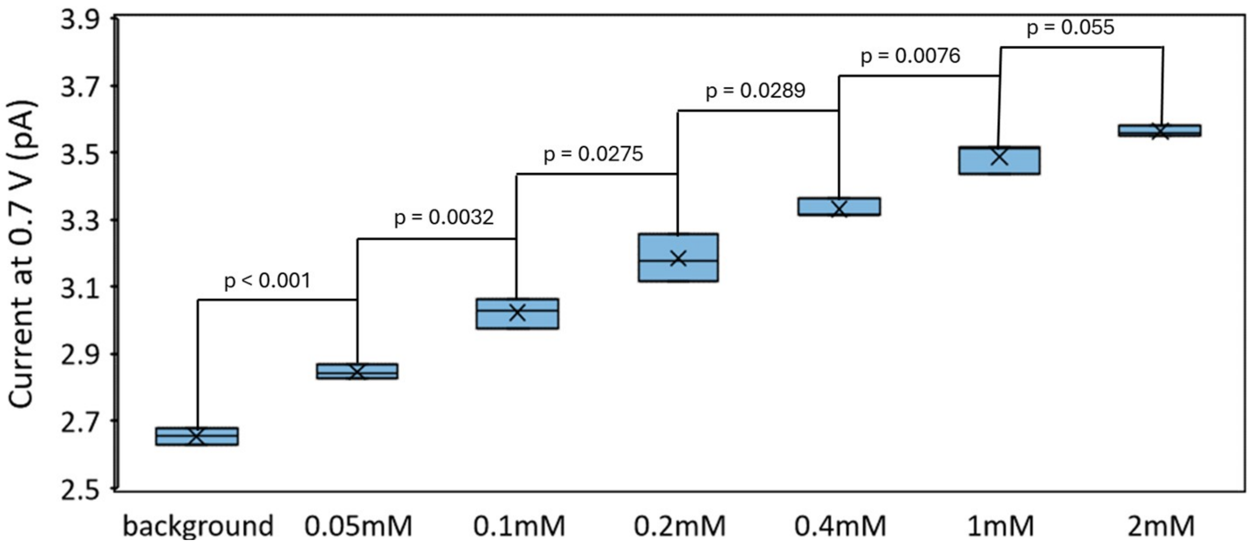

Figure S3. Box plot and two-sample t-test for current at +0.7 V vs. Ag/AgCl/1 M KCl from cyclic voltammograms of blank and glutamate solutions of different concentrations. Two-sample t-test was performed using MatLab to test if the current from between the blank and the added lowest glutamate concentration, as well as between adjacent glutamate concentrations is significantly different from each other. Most of them showed a very low p value, which means there is a significant difference in the current from glutamate solutions of different concentrations.

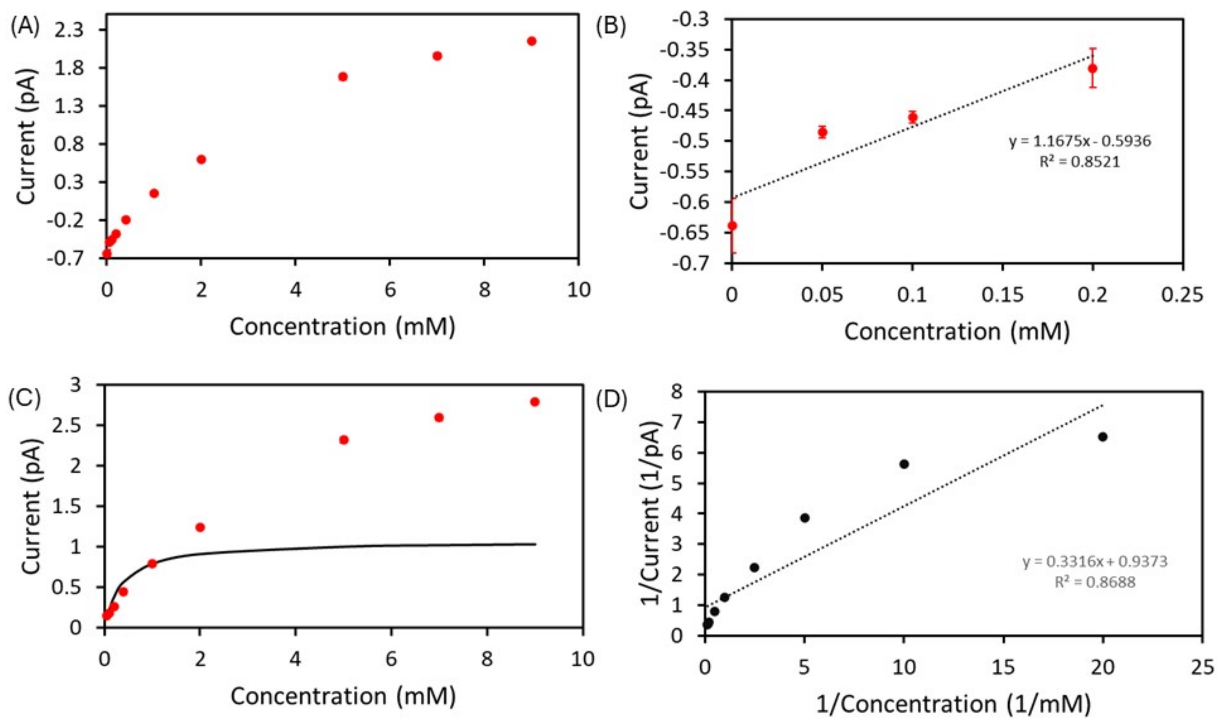

Figure S4. (A) Glutamate detection current on a second GluOx-modified Pt nanoelectrode as a function of the glutamate concentration; Pt nanoelectrode was shown in Figure 8A. Y axis is the current measured at +0.7 V vs. Ag/AgCl/1M KCl from forward CVs in Figure 8B and x-axis is the concentration of glutamate. (B) The calibration curve at low concentration range (up to 200 μM), where a linear current-concentration response was observed although the R^2 is not as high as the first Pt nanoelectrode. This electrode showed a sensitivity of 1.1675 pA/mM and an area-normalized sensitivity of 1.437×10^{-5} nA μM^{-1} μm^{-2}. (C) The fitting of the background-subtracted experimental current-concentration curve (red square) to Michaelis-Menten curve (black solid line). (D) A plot of $1/i$ vs $1/c$ for the calculation of Michaelis-Menten parameters with experimental data shown as black solid dot and best linear fit as dashed line. The intercept of this curve is $1/i_{max}$, and the slope of this curve is K_m/i_{max}. Based on slope and intercept, i_{max} was calculated to be 1.067 pA and K_m was calculated to be 0.354 mM. It is worth noting that the Michaelis-Menten curve did not fit well for this calibration curve. As shown by the error bar of blank solution (Figure S4B), a large current variation was observed, which might limit accurate measurements of glutamate at low concentrations. In addition, the presence of PEI on this Pt nanoelectrode surface could possibly affect the analytical performance of this GluOx-modified Pt nanoelectrode, resulting in current-concentration curve not fitted well with Michaelis-Menten equation.

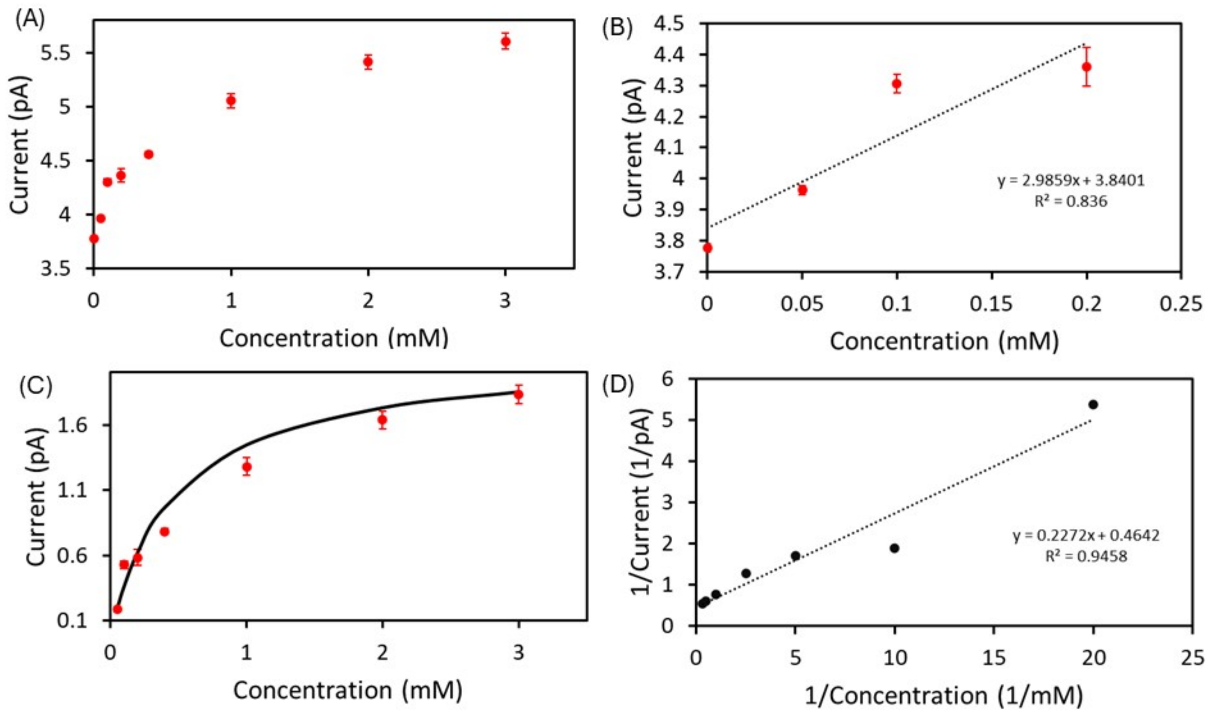

Figure S5. A) Glutamate detection current on a third GluOx-modified Pt nanoelectrode as a function of the glutamate concentration; Pt nanoelectrode was shown in Figure 8C. Y axis is the current measured at +0.7 V vs. Ag/AgCl/1M KCl from forward CVs in Figure 8D and x-axis is the concentration of glutamate. (B) The calibration curve at low concentration range (up to 200 µM), where a linear current-concentration response was observed although the R^2 is not as high as the first Pt nanoelectrode. This electrode showed a sensitivity of 2.986 pA/mM, and an area-normalized sensitivity of 3.14×10^{-5} nA μM^{-1} μm^{-2}. (C) The fitting of the background-subtracted experimental current-concentration curve (red square) to Michaelis-Menten curve (black solid line). (D) A plot of $1/i$ vs $1/c$ for the calculation of Michaelis-Menten parameters with experimental data shown as black solid dot and best linear fit as dashed line. The intercept of this curve is $1/i_{max}$, and the slope of this curve is K_m/i_{max}. Based on slope and intercept, i_{max} was calculated to be 2.154 pA, K_m was calculated to be 0.489 mM.

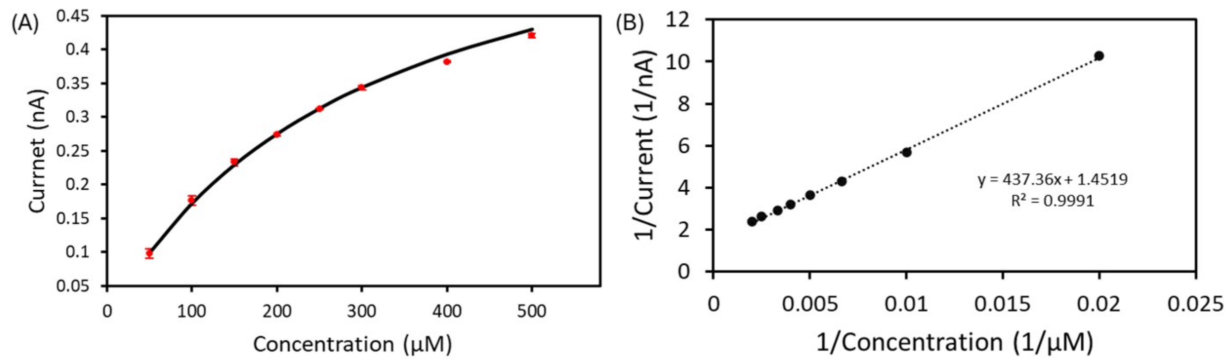

Figure S6. Michaelis-Menten parameters calculation for carbon fiber microelectrode. (A) The fitting of the background-subtracted experimental current-concentration curve (red square) to Michaelis-Menten curve (black solid line). (B) A plot of $1/i$ vs $1/c$ for the calculation of Michaelis-Menten parameters with experimental data shown as black solid dot and best linear fit as dashed line. The intercept of this curve is $1/i_{max}$, and the slope of this curve is K_m/i_{max}. Based on slope and intercept, i_{max} was calculated to be 0.689 nA, K_m was calculated to be 301.2 μM.