Supporting Information

Mechanism of an Enzymatic Reaction-Induced SERS Transformation for the Study of Enzyme-Molecule Interfacial Interactions

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Figure S1. SEM image of the silver nanoparticle-decorated substrate. The surface of the glass slide was covered with 70 nm silver nanoparticles. The scale bar is 100 nm.
Study of the enzymatic reaction kinetics

Herein, the Michaelis-Menten model was used to account for the observed dependence of the SERS intensity on the glucose concentration. The model assumes the following reaction mechanism:\textsuperscript{1-5}

\[ E + S \rightleftharpoons ES \rightarrow E + P \]

where E, S, ES and P are the enzyme, substrate (in this case, glucose), enzyme-substrate complex and product, respectively. The mechanism assumes that a quasi-equilibrium is established between the enzyme-substrate complex and the free enzyme and free complex, as implied by the double arrow. Subsequently, the enzyme-substrate complex concentration can be approximated by the following equation:

\[
\frac{[E][S]}{[ES]} = K_M \tag{1}
\]

Note that in the equation \([E]=[E]_o-[ES]\), in which \([E]_o\) is the initial enzyme concentration, one can substitute for \([E]\) in Eq. 1 to derive the following equation:

\[
[ES] = \frac{[E]_o[S]}{K_M + [S]} \tag{2}
\]

The quantity proportional to the enzyme complex concentration \([ES]\) was calculated using the decrease in the intensity of the 998 cm\(^{-1}\) band as a function of glucose concentration. During the reaction, it could be easily concluded from Fig. S3 that the glucose concentration \([S]\) is inversely proportional to the SERS intensity of the band at 998 cm\(^{-1}\) \((I_c)\). Therefore, \([S]\) is proportional to \(I_o-I_c\). Therefore, we obtain the
relationship $[ES] \propto \frac{I_o - I_c}{I_o}$, in which $I_o$ is the SERS intensity of the 998 cm$^{-1}$ band at zero glucose concentration and $I_c$ is the SERS intensity of that band at concentration $c$.

Accordingly, Eq. (2) can be rewritten as:

$$\frac{I_o - I_c}{I_o} = \sigma [E]_o [S] \frac{1}{K_M + [S]}$$  \hspace{1cm} (3)

in which $\sigma$ is a constant of proportionality (with dimensions M$^{-1}$). Fitting Eq. (3) to the data given in Fig. S3 produced the fit from which the value $K_M = 8.2 \times 10^{-6}$ M was derived.

Figure S2. Study of the enzymatic reaction kinetics using the Michaelis-Menten model
Figure S3. Normalized SERS spectra of MBA anchored to AgNP-coated glass slides upon exposure to a $10^{-6}$ M glucose solution with (B) and without (A) a deoxygenation process with increasing immersion time.
Figure S4. The SERS spectra of Ag/MBA with (a) immersion of the Ag/MBA complex in a mixed solution of Gox and glucose and (b) immersion of the Ag/MBA/Gox complex in a glucose solution (c).
Figure S5. The SERS relative intensity ratio of the bands $I_{998}/I_{1077}$ (A) and $I_{1020}/I_{1077}$ (B) as a function of the glucose concentration, where the threshold line indicates the position 3 standard deviations from the value for the blank sample.
References


