# Redox molecule based SERS sensors: Supplementary Information

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## I. MODEL FOR THE ELLIPSOMETRIC STUDY OF PAH-OS/PVS MLS

Ellipsometric studies are not straightforward when, as is our case, the optical constants $n$ and $k$ are not known, the film thickness is also unknown, and the latter corresponds to an ultrathin layers of thickness $l \ll \lambda$. Here $\lambda$ is the wavelength of light. The situation is particularly critical when $l < 20$ nm, as is our case, because of the large correlations existent between the unknown parameters, leading to large uncertainties in the treatment of the ellipsometric data. In fact, in a standard ellipsometric study one obtains two experimental inputs (the so-called $\psi$ and $\Delta$ parameters, related to the relative amplitude and phase, respectively, of the s and p-reflected waves), but needs to extract three material properties, $l$, $n$ and $k$. A variable angle spectroscopic ellipsometer adds additional information by measuring in a large spectral range, and at different incidence angles. Measurements at different wavelengths are useful because one may be able to define a region were, e.g. there cannot be absorption and hence $k = 0$. This allows to obtain $l$, and then the complex index of refraction can be extracted for all wavelengths. If, however, one cannot exclude residual absorption at any wavelength, a spectroscopic measurement is still powerfull through the use of models that can describe the dispersion of the optical constants, for example below critical points in the band structure of solids, or below resonant transitions in molecules. Once this is done, several measurements at different wavelengths can be used to derive the reduced number of parameters that define the model used, and $l$. In all cases the measurements at many incidence angles provide arguments of consistency, and allow measurements in conditions in which $\psi$ and $\Delta$ can be extracted with minimum experimental uncertainty.

If, however, none of these approaches provides self-consistent and reasonable outputs, alternative strategies need to be considered. This is specifically the case when the films are very thin, and the optical response is complex because of the presence of different kinds of molecules, or with different chemical enviroments, or because of the presence of residual absorption of unknown origin. One of these strategies is the "multiple sample analysis", by which one studies a set of samples of different thickness, and assuming the *same* optical response for all of them seeks a solution that consistently accounts for the $\psi$ and $\Delta$ parameters determined for the samples with different $l$, at all wavelengths and for all incidence angles. One such case applies to the study of multilayers, were one may assume that the optical response is independent of the number of bilayers. This approach, that needs to be critically analysed in each case, is particularly appropriate and needed when layer thicknesses in the range or lower to 10-20 nm are studied.[1]

The data presente in the paper were derived using this latter procedure. In fact, we observed that any other approach leads to local minima in the approximation routines with solutions of similar quality that depend on the initial conditions proposed for the unknown parameters. The multiple sample approach, on the contrary, led to perfectly stable solutions. For this purpose the procedure is as follows. We propose a model consisting of five Gauss oscillators given by $A_n B_n E_n / (E_n^2 - E^2 - i B_n E)$, with $A_n$ the amplitude, $B_n$ the width, and $E_n$ the spectral position of oscillator $n$, and $E$ the energy of the exciting light. Then, we fit the oscillator parameters $A_n$, $B_n$, $E_n$ and the film thickness $l$ by calculating ellipsometric parameters $\psi$ and $\Delta$ for all wavelengths using the Gauss model and comparing the output with the experimental values through a figure of merit. This procedure is repeated iteratively until the agreement between calculated and experimental values is within set limits. We recall that this is done *simultaneously* for the five studied samples. The parameters derived for the Gauss-oscillator model are given in Table. I. These parameters were used to evaluate the Gauss oscillator model presented in Fig. 3 with solid lines.

|  | $E_n$ | $A_n$ | $B_n$ |
|---|---|---|---|
| Gauss$_1$ | 4.210 | 0.3278 | 0.490 |
| Gauss$_2$ | 3.566 | 0.2918 | 1.054 |
| Gauss$_3$ | 2.805 | 0.1769 | 0.694 |
| Gauss$_4$ | 2.652 | 0.0446 | 0.252 |
| Gauss$_5$ | 2.347 | 0.1963 | 0.388 |

TABLE I: Coefficients for the Gauss oscillator model used in the ellipsometric investigation (see text for details). $E_n$ and $B_n$ are expressed in $eV$, while $A_n$ is dimensionless.

## II. ASSIGNMENT OF FLAVIN RAMAN VIBRATIONAL MODES IN AG-NANOCAVITIES

A tentative assignment of the observed vibrations of the two forms of the flavin molecule can be done based on the experimental data and calculations reported by Bowman and Spiro[2] for flavoproteins, and on the flavin SERS spectra study as a function of pH reported by Xu et al.[3]. This assignment, together with the measured mode frequencies, are given in Table II.

| reduced Flavin | semiquinone Flavin | assignment |
|:---:|:---:|:---:|
| 1347 | 1353 | $\nu CN$, $\delta CH_3$ |
| - | 1373 | $\nu CN$, $\nu CC$, $\delta CH_3$ |
| 1400 | - | $\nu CC$, $\delta CH_3$ |
| 1458 | 1449 | $\nu CN$ |
| 1496 | 1499 | $\nu CN$, $\nu CC$ |
| - | 1523 | $\nu CN$, $\nu CC$ |
| 1539 | - | $\nu CN$, $\nu CC$ |
| 1576 | 1576 | $\nu CC$ |
| - | 1611 | $\nu CN$, $\nu CO$ |
| 1623 | - | $\nu CN$, $\nu CO$ |

TABLE II: Observed Flavin Raman modes corresponding to its reduced and semiquinone oxidation states and their assignments according to Refs.[2,3]. $\nu(\delta)$ stand for stretching (bending) vibrations.

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2 Bowman, W. D.; Spiro, T. G. *Biochemistry*, **20**, 3313 (1981).

3 Xu, J.; Birke, R. L.; Lombardi, J. R. *J. Am. Chem. Soc.*, **109**, 5645 (1987).