

## Raman Spectroelectrochemical Study on Bioactive Molecules

CAO Xiao-Wei<sup>\*</sup>, YANG Hai-Feng, WANG Zhe-Su  
MENG Xiao-Yun, WU Xia-Qin, ZHANG Zong-Rang

(Dept. of Chem., Shanghai Teachers Univ., Shanghai 200234, China)

E-mail: xwcao@shtu.edu.cn

CLC Number: O 646; O 433

Document Code: A

**Detailed abstract:** Electron-transfer reaction is known to be one of the key reactions for generating biological functions. Mechanism revelation at a molecular level of such kind reactions is to be very helpful for us to understand life essence. In fact, surface enhanced Raman scattering (SERS) is one of the most powerful tools for the study on metal-electrolyte and metal-vacuum interfaces since 1970's. Moreover, Raman spectroscopic study in enzymology has provided attractive results during last twenty-five years. For the study of electron-transfer reaction mechanism of some oxidoreductases and SERS of some other biological macromolecules, an electrochemical *in situ* Raman spectroscopic technique was established in author's lab and some research works have been done on it in the past two years. A brief review of these works is given in this paper.

The electrochemical *in situ* Raman spectroscopic measurements were carried out using a Super LABRAM Raman spectrometer (Dilor, France) coupled with a CHI604A Electrochemical Analyzer (CH Instr., USA). A Teflon spectroelectrochemical cell with a quartz plate window was designed for the *in situ* measurements. The working electrode was pretreated with oxidation-reduction cycles for each measurement. The electrolyte solutions were purged with nitrogen prior to all measurements, and all the measurements were carried out under the nitrogen atmosphere.

Copper, zinc superoxide dismutase (SOD) is an important oxidoreductase for organism metabolism. The established spectroelectrochemical technique was first used to characterize the

Received date: 20 Nov. 2000

\* Corresponding author

Foundation item: Project supported by Youth Science and Technology "Rising Star" Foundation of Shanghai Science and Technology Committee (No.00QA14017)

cyclic voltammetric process of SOD at L-cysteine modified gold electrode as well as the process of electrochemical modification of L-cysteine molecules on a gold electrode. The obtained Raman spectra reveal that the L-cysteine modified gold electrode improves effectively the reversibility of electron-transfer reactions of SOD.

Besides L-cysteine molecules, it was interesting that adenine was also an effective electron-transfer promoter for SOD at gold electrode. A strong peak at  $355\text{ cm}^{-1}$  can be observed in the Raman spectrum of adenine molecules adsorbed on gold electrode. It was inferred that the peak maybe related to the chemical interaction between adenine molecules adsorbed and gold electrode surface. As shown in Fig. 1, for the mixture of SOD and adenine at gold electrode under a polarization potential  $55\text{ mV}$  (vs. SCE), both the characteristic Raman lines of SOD and adenine molecules appeared. Therefore it was reasonable to conclude that SOD and adenine molecules should be co-adsorbed on gold electrode surface under such a potential, which is slightly lower than the reduction peak potential of SOD on adenine-modified gold electrode.

Moreover, two new peaks appeared remarkably at  $445\text{ cm}^{-1}$  and  $610\text{ cm}^{-1}$  are likely to be related to the active site of SOD. It suggests that the co-adsorption mechanism of SOD and adenine molecules on the gold electrode surface results in effective approaching of the active site of SOD to the electrode surface.

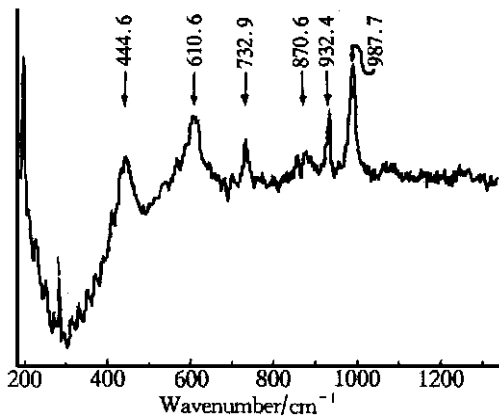


Fig. 1 Observed electrochemical *in situ* SERS spectra of the mixture of SOD ( $0.13\text{ mmol/L}$ ) and adenine ( $0.5\text{ mmol/L}$ ) at gold electrode under the potential  $55\text{ mV}$  (vs. SCE)

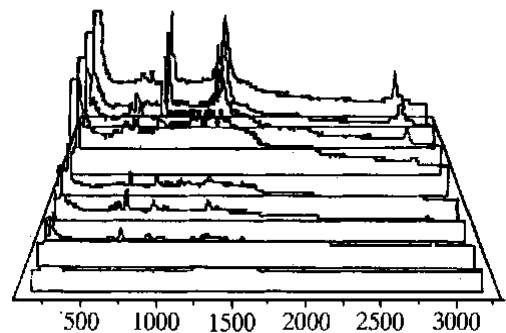


Fig. 2 Electrochemical *in situ* Raman spectra of the adsorption model of NAD on roughening silver electrode. The corresponding potential range:  $0.4\text{ V} \sim 0.2\text{ V}$  (vs. SCE)

As shown in Fig. 2, adsorption of nicotinamide adenine dinucleotide (NAD) on silver electrode was investigated. The obtained spectra depict that under the polarization condition, NAD adsorbs on a silver electrode with an extended conformation, in which the flexibility of bound phosphate provides a degree of freedom for the adenine and nicotinamide moieties to change their orientations. In the potential region from  $0.4\text{ V}$  to  $0.2\text{ V}$  (vs. SCE), the adenine moiety would

adopt a perpendicular orientation in which the no. 7 nitrogen atom from adenine ring and amino group are coordinated to the electrode surface. At more negative potential from 0.1 V ~ 0.2 V, the adenine moiety adsorbs on silver electrode mainly through a flat orientation with the adenine ring as the coordination site.

The Raman spectroelectrochemical studies for DNA and adenosine monophosphate (AMP) on the silver collosol were under consideration in authors' lab recently. The observed spectra depicted that only very low level of fluorescence interference was shown in the SERS of AMP and DNA via the adsorption on the nanoparticles of silver even in very low concentration of AMP and DNA solution.

**Key words :** Bioactive molecules , Electrochemical *in situ* , Raman spectroscopy

**Acknowledgement :** The financial support from Shanghai Science and Technology committee (No.00QA14017) is greatly appreciated.

## References

- [1] Wu X Q, Meng X Y, Wang Z S, et al. Study on the direct electron transfer process of superoxide dismutase [J]. *Bioelectrochemistry & Bioenergetics*, 1999 : 48 , 227 ~ 231.
- [2] Wu X Q, Meng X Y, Wang Z S, et al. Study on the ET process of SOD at cysteine modified gold electrode [J]. *Chem. Lett.* , 1999 : (12) : 1271 ~ 1272.
- [3] Cao X W, Meng X Y, Wang G H, et al. *In situ* Raman Spectroscopic Study on Electrode [J]. *Chinese Journal of Light Scattering*, 1999 : 11(4) : 316 ~ 321.

# 生物活性分子的拉曼光谱电化学研究

曹晓卫<sup>\*</sup>, 杨海峰, 王浙苏, 孟晓云, 吴霞琴, 章宗穰

(上海师范大学化学系, 上海 200234)

**摘要:** 本文概述了采用电化学现场拉曼光谱技术研究氧化物歧化酶在 L-半胱氨酸修饰金电极表面的电子迁移反应以及腺嘌呤共存条件下超氧化物歧化酶在金电极表面的电子迁移反应和不同电位下银电极表面烟酰胺腺嘌呤二核苷酸的吸附等体系的反应吸附特性. 所得结果对于分析和研究生物活性分子电化学过程机理具有重要意义.

**关键词:** 生物分子; 电化学现场; 拉曼光谱学