



Application Note AN-EC-033

利用联用电化学-拉曼光谱法研究一个模型系统

Example of the reduction of 4-nitrothiophenol

The combination of Raman spectroscopy and electrochemistry, known as hyphenated EC-Raman, is a powerful tool for researchers. More information can be extracted from this combination than can be gained from either technique alone.

4-nitrothiophenol (4-NTP) is a strongly Raman-active molecule that is also electrochemically active. At mildly cathodic potentials, 4-NTP undergoes a six-electron proton-coupled reduction to 4-aminothiophenol (4-ATP).

Therefore, the reduction can easily be monitored using traditional electrochemical techniques (e.g., cyclic voltammetry) but also through the changes to the Raman spectrum. In the past, 4-NTP has served as a model system for studying the SERS (surface-enhanced Raman spectroscopy) effect and has relevance for example in corrosion [1] and electrocatalysis [2] applications.

This Application Note presents a walkthrough of a hyphenated EC-Raman experiment on 4-NTP.

EXPERIMENTAL

A Metrohm EC-Raman solution was used consisting of a VIONIC powered by INTELLO potentiostat and Metrohm i-Raman Plus 532H system. A specialized cell for EC-Raman was employed (RAMAN ECFC, RedoxMe). The cell consists of three electrodes: an Ag/AgCl reference electrode, Pt wire counter electrode, and an Au disk working electrode.

A SERS substrate was prepared in-situ by electrochemically roughening the Au disk electrode. The 4-NTP was immobilized in a surface monolayer, prepared by drop casting onto an electrochemically roughened Au SERS

substrate. The surface was thoroughly rinsed with ethanol before use. The cell was then filled with 0.05 mol/L H_2SO_4 .

All Raman spectra were acquired with an i-Raman Plus 532H controlled by SpecSuite software. A potential step experiment was performed where the potential was stepped from 0.2 V to -0.55 V in 0.05 V, 40-second steps. Raman spectra were acquired at each potential step. The Raman spectra were acquired at 100% laser power with a 10 s integration time and averaged three times.

RESULTS

The cyclic voltammogram (CV) of the 4-NTP monolayer is shown in **Figure 1**. This provides information about which potentials will be needed later in the potential step experiment.

The CV also reveals a single, irreversible cathodic peak at approximately -0.3 V vs Ag/AgCl. This peak corresponds to the complete reduction of 4-NTP to 4-ATP (**Figure 1**, insert).

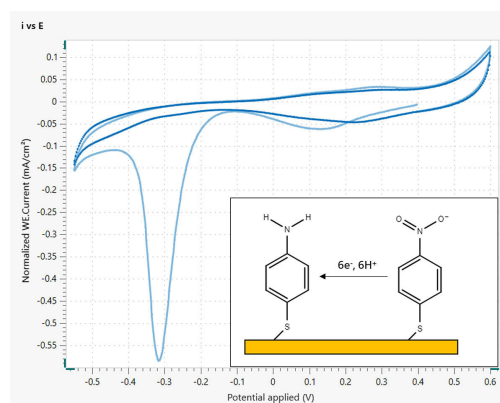


Figure 1. Cyclic voltammogram of 4-NTP adsorbed onto a roughened Au surface in 0.05 mol/L sulfuric acid.

The electrochemical response recorded during the potential step experiment is shown in **Figure 2**. VIONIC sends TTL pulses to the i-Raman plus system which triggers the measurement of a new spectrum at the beginning of each step. For clarity purposes, only the first and last recorded Raman spectrum (corresponding to 0.2 V and -0.55 V, respectively) are shown in **Figure 3**.

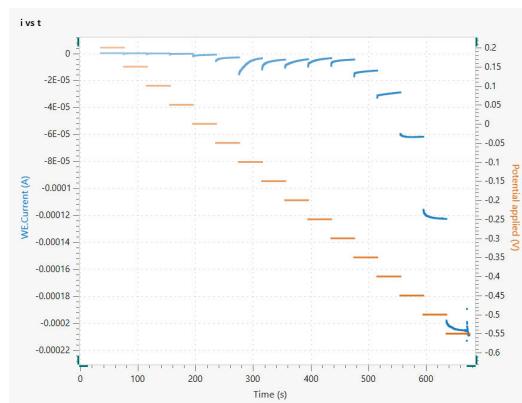


Figure 2. The electrochemical response of the 4-NTP monolayer recorded during the potential Step experiment in 0.05 mol/L sulfuric acid.

RESULTS

The transformation of 4-NTP to 4-ATP is most easily recognized by the loss of the NO_2 stretching mode at 1337 cm^{-1} . The C-C stretching mode at 1572 cm^{-1} in 4-NTP also shifts to higher wavenumbers in 4-ATP (1578 cm^{-1}). A full assignment of the observed bands is provided in **Table 1**.

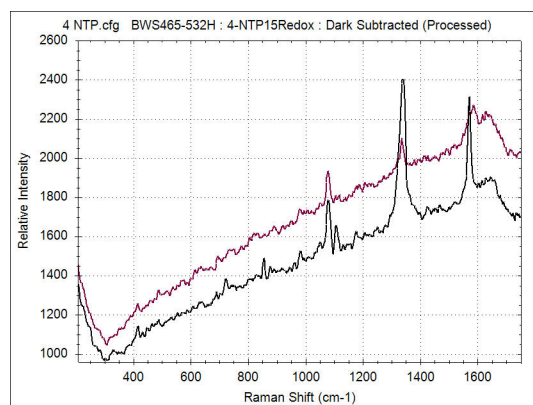


Figure 3. Raman spectra acquired at the first and last potential step during the potential step experiment (Figure 2).

Table 1. Raman shifts and associated vibration modes [3,4] of 4-NTP and 4-ATP as measured during this experiment.

Compound	Raman Shift (cm ⁻¹)	Vibration Mode
4-NTP	1078	C-H bending
	1105	C-H bending
	1337	NO ₂ stretching
	1572	C-C stretching
4-ATP	1078	C-H bending
	1578	C-C stretching

CONCLUSION

A walkthrough of a model experiment for EC-Raman was shown using the example of 4-nitrothiophenol. While the molecule itself is useful in testing new materials for the SERS effect, EC-Raman presents researchers with a convenient way to track the reduction of the

molecule.

In general, hyphenated EC-Raman gives excellent molecular insights into electron-transfer reactions occurring in organic molecules.

REFERENCES

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CONFIGURATION



VIONIC

VIONIC 是我们的新一代恒电位仪 / 恒电流仪, 由 Autolab 的新 INTELLO 软件提供动力。

相比目前市场上任何单一仪器, VIONIC 提供了全面的组合规格。

- 顺从电压: $\pm 50\text{ V}$
- 标准电流 $\pm 6\text{ A}$
- EIS 频率: 达 10 MHz
- 采样间隔: 低至 $1\mu\text{s}$

VIONIC 的价格中通常还包括大多数其他仪器产生的额外费用, 例如:

- 电化学阻抗谱 (EIS)
- 可选浮动配件
- 第二测量电极 (S2)
- 模拟扫描



i-Raman Plus 532H

该 i-Raman[®] Plus 532H 是我们屡获殊荣的 i-Raman 便携式拉曼光谱仪系列的一部分, 其采用我们创新的智能光谱仪技术。这款便携式拉曼光谱仪使用了具有高量子效率、TE 冷却功能和高动态范围的 CCD 阵列检测器, 即使集成时间长达 30 分钟, 也能提供出色的低噪声性能。因此, 还可以测量较弱的拉曼信号。

i-Raman Plus 532H 具有宽光谱范围和高分辨率的独特组合, 其配置允许在 65 cm^{-1} 至 3400 cm^{-1} 之间进行测量。该系统基础面积小, 结构形式轻巧并且能耗低, 故此可随时随地进行研究级别的拉曼分析。该 i-Raman Plus 配备有便于采样的光纤探头, 并可以与一个比色皿支架、一个视频显微镜、一个带探头支架的 XYZ 平移台、我们公司内部的 BWIQ[®] 多变量分析软件和鉴定软件 BWID[®] 搭配使用。有了 i-Raman Plus, 您始终可以使用高精度拉曼解决方案进行定性和定量分析。