

Application Note AN-EC-033

利用用化学-拉曼光法研究一个模型系

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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 an i-Raman Plus 532H system (B&W TEK). 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 BWSpec 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 using the BWSpec Timeline plugin.

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).

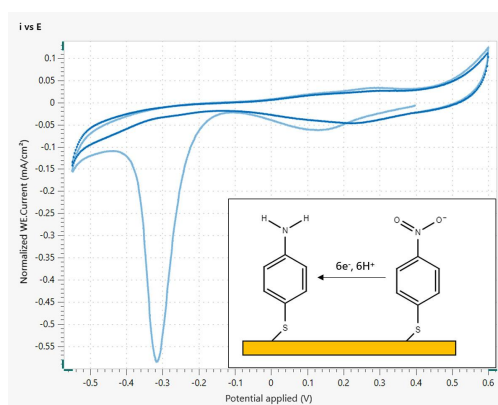


Figure 1. Cyclic voltammogram of 4-NTP adsorbed onto a roughened Au surface in 0.05 mol/L sulfuric acid.

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**.

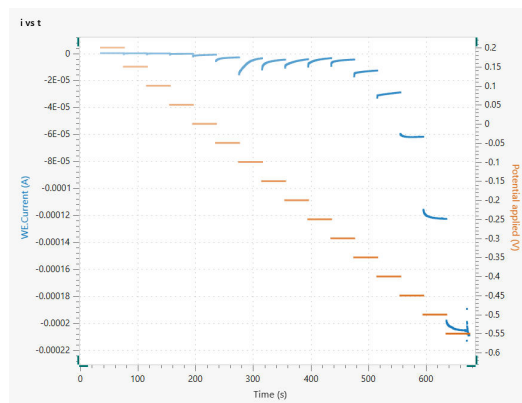


Figure 2. The electrochemical response of the 4-NTP monolayer recorded during the potential Step experiment in 0.05 mol/L sulfuric acid.

The transformation of 4-NTP to 4-ATP is most easily recognized by the loss of the NO₂ 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**.

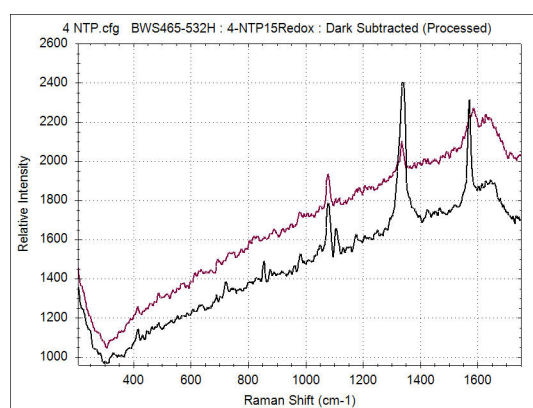


Figure 3. Raman spectra acquired at the first and last potential step during the potential step experiment (Figure 2).

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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CONTACT

瑞士万通中国
北京市海淀区上地路1号院
1号楼7702
100085 北京

marketing@metrohm.com.cn

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