Utilizing hyphenated EC-Raman to study a model system

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).
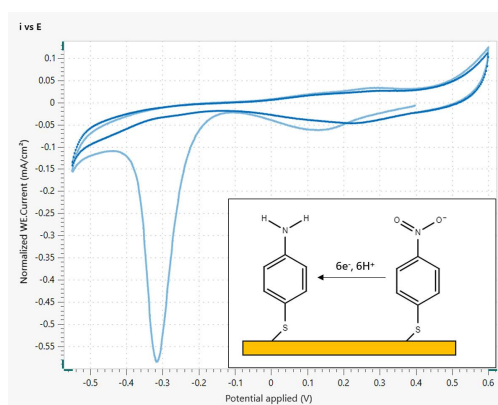

Figure 1. Cyclic voltammogram of 4-NTP adsorbed onto a roughened Au surface in 0.05 mol/L sulfuric acid.

Ω Metrohm

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.
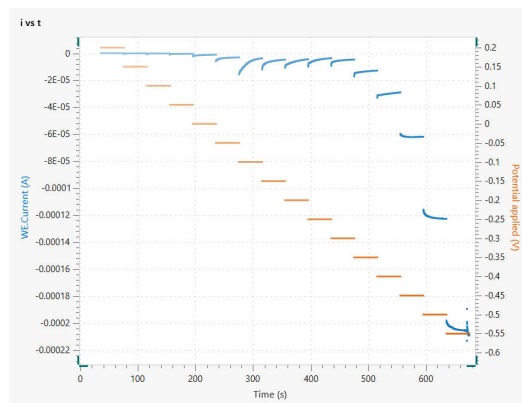

Figure 2. The electrochemical response of the 4-NTP monolayer recorded during the potential Step experiment in 0.05 mol/L sulfuric acid.

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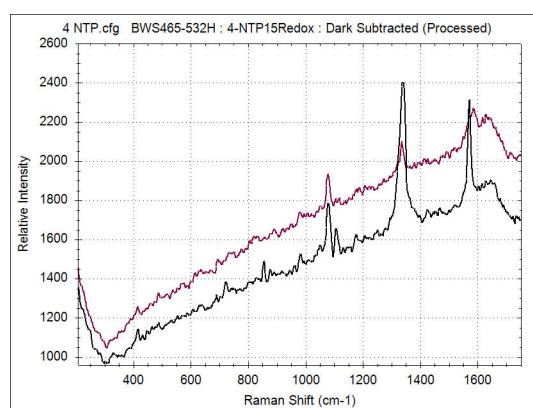

Figure 3. Raman spectra acquired at the first and last potential step during the potential step experiment (Figure 2).

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

Ω Metrohm

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

1. Morávková, Z.; Dmitrieva, E. Structural Changes in Polyaniline near the Middle Oxidation Peak Studied by in Situ Raman Spectroelectrochemistry. *Journal of Raman Spectroscopy* 2017, *48* (9), 1229–1234. https://doi.org/10.1002/jrs.5197.

2. Dong, J.-C.; Zhang, X.-G.; Briega-Martos, V.; et al. In Situ Raman Spectroscopic Evidence for Oxygen Reduction Reaction Intermediates at Platinum Single-Crystal Surfaces. *Nat Energy* 2019, 4 (1), 60–67. https://doi.org/10.1038/s41560-018-0292-z.

3. Lopez-Ramirez, M. R.; Aranda Ruiz, D.; Avila Ferrer, F. J.; et al. Analysis of the Potential Dependent Surface-Enhanced Raman Scattering of p-Aminothiophenol on the Basis of MS-CASPT2 Calculations. *J. Phys. Chem. C* 2016, *120* (34), 19322–19328. https://doi.org/10.1021/acs.jpcc.6b05891.

4. Tabatabaei, M.; Sangar, A.; Kazemi-Zanjani, N.; et al. Optical Properties of Silver and Gold Tetrahedral Nanopyramid Arrays Prepared by Nanosphere Lithography. *J. Phys. Chem. C* 2013, *117* (28), 14778–14786. https://doi.org/10.1021/jp405125c.

CONTACT

メトロームジャパン株式会社
143-0006 東京都大田区平和島6-1-1
null 東京流通センター アネックス9階

metrohm.jp@metrohm.jp

Ω Metrohm

CONFIGURATION

VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new **INTELLO** software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage: ± 50 V
- Standard current ± 6 A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1 µs

Also included in **VIONIC's** price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan

Ω Metrohm

i-Raman Plus 532H

i-Raman® Plus 532H は、弊社の革新的かつインテリシェントなスヘクトロメーターテクノロシーを備えた i-Raman 携帯型ラマンスヘクトロメーターの受賞歴のあるシリースの構成要素てす。この携帯型ラマンスヘクトロメーターは、高い量子効率、TE 冷却、ならひに高いタイナミックレンシを備えた CCD アレイ検出器を用い、積分時間てさえ最長 30分、低ノイスの傑出した性能を提供します。こうして、弱いラマン信号も測定することかてきます。

i-Raman Plus 532H は、65 cm^{-1} から 3400 cm^{-1} まての測定を可能にするコンフィクレーションを有する幅広いスヘクトル範囲と高分解能のユニークな組み合わせを特徴としています。 システムの小さな底面、軽量構造、そして低消費電力により、とてもラマン分析を研究レヘルて実施することかてきます。i-Raman Plus には、サンフル採取を簡単にする光ファイハーフローフか装備されており、キュヘットホルター、ヒテオマイクロスコーフ、フローフホルター付き XYZ スライトテーフル、ならひに弊社独自の多変量解析ソフトウェア BWIQ® およひ同定ソフトウェア BWID® と共に使用することかてきます。i-Raman Plus により、品質分析およひ定量分析のための高精度のラマンソリューションを常に使用することかてきます。

Ω Metrohm