

Application Note AN-EC-033

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 a 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).

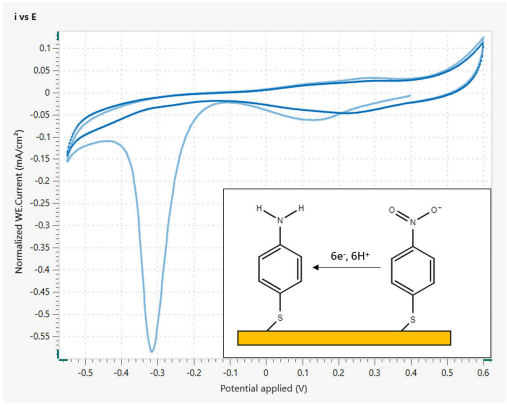


Figure 1. Cyclic voltammogram of 4-NTP adsorbed onto a roughened Au surface in 0.05 mol/L sulfuric acid.

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.

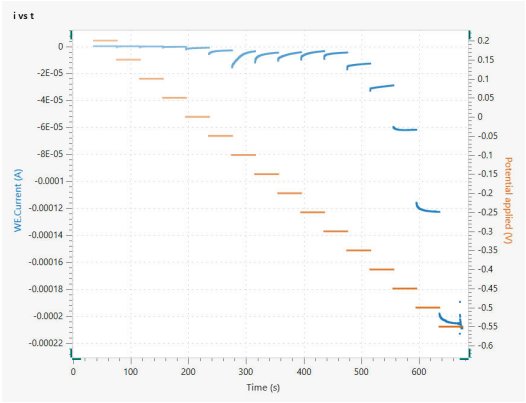


Figure 2. The electrochemical response of the 4-NTP monolayer recorded during the potential Step experiment in 0.05 mol/L sulfuric acid.

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.

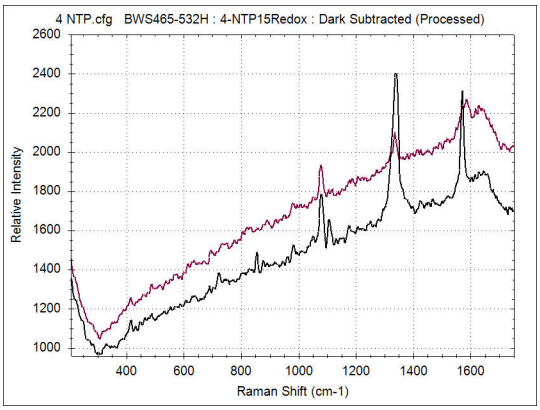


Figure 3. Raman spectra acquired at the first and last potential step during the potential step experiment (Figure 2).

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.

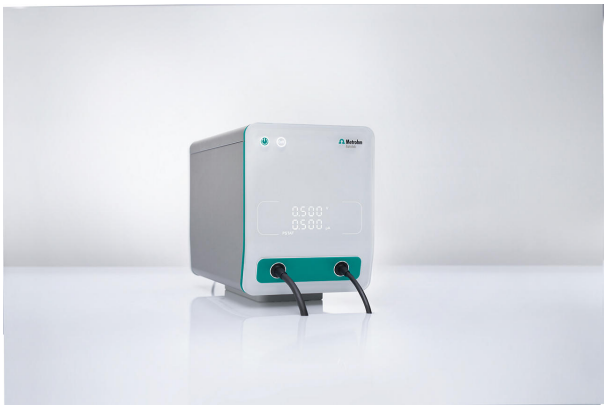
REFERENCES

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

Metrohm Middle East FZC
E2-05 SAIF Zone
120747 Sharjah, UAE
info@metrohm.ae

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



i-Raman Plus 532H Portable Raman Spectrometer

The i-Raman® Plus 532H is part of our award-winning series of i-Raman portable Raman spectrometers powered by our innovative intelligent spectrometer technology. Using a high-quantum-efficiency CCD array detector with TE cooling and high dynamic range, this portable Raman spectrometer delivers excellent performance with low noise, even at integration times of up to 30 minutes, making it possible to measure weak Raman signals.

The i-Raman Plus 532H features the unique combination of wide spectral range and high resolution with configurations which allow measurements from 65 cm^{-1} to 3,400 cm^{-1}. The system's small footprint, lightweight design, and low power consumption ensure research-grade Raman analysis capabilities at any location. The i-Raman Plus is equipped with a fiber probe for easy sampling, and can be used with a cuvette holder, a video microscope, an XYZ positioning stage with a probe holder, as well as our proprietary BWIQ® multivariate analysis software and BWID® identification software. With the i-Raman Plus, you always have a high precision Raman solution for qualitative and quantitative analysis.