

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 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

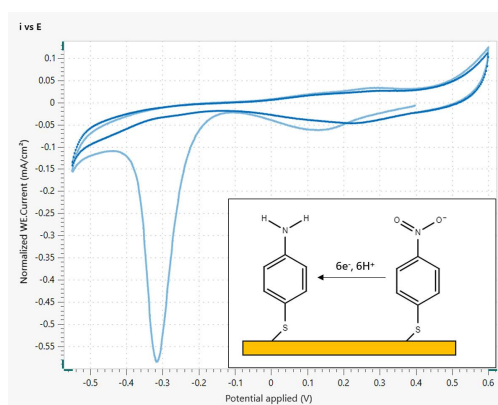
thoroughly rinsed with ethanol before use. The cell was then filled with 0.05 mol/L  $\text{H}_2\text{SO}_4$ .

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.

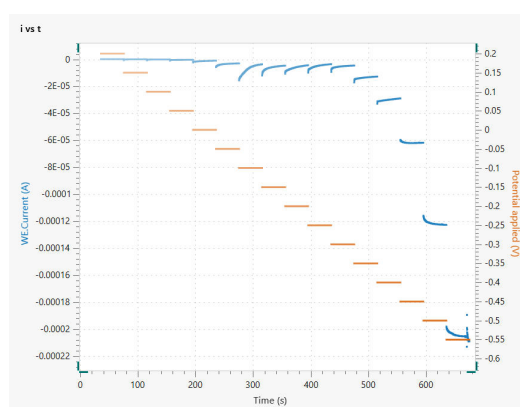
The CV also reveals a single, irreversible cathodic peak at approximately -0.3 V vs Ag/AgCl. This peak corresponds to the complete reduction of 4-NTP to 4-ATP (**Figure 1**, insert).



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

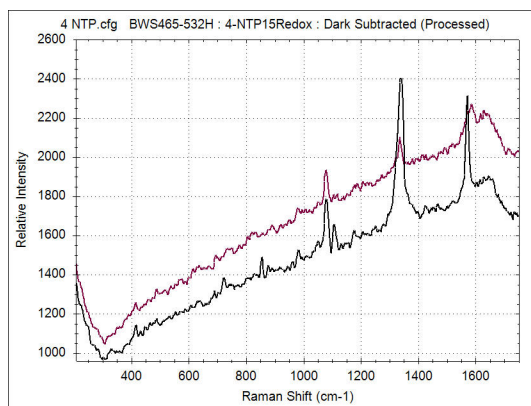
The electrochemical response recorded during the potential step experiment is shown in **Figure 2**. VIONIC sends TTL pulses to the i-Raman plus system which triggers the measurement of a new spectrum at the beginning of each step.

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 NO<sub>2</sub> stretching mode at 1337 cm<sup>-1</sup>. The C-C stretching mode at 1572 cm<sup>-1</sup> in 4-NTP also shifts to higher wavenumbers in 4-ATP (1578 cm<sup>-1</sup>). 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 <sup>-1</sup> )	Vibration Mode
4-NTP	1078	C-H bending
	1105	C-H bending
	1337	NO <sub>2</sub> 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 Italiana Srl  
Via G. Di Vittorio, 5  
21040 Origgio (VA)

[info@metrohm.it](mailto:info@metrohm.it)

## CONFIGURATION



### VIONIC

VIONIC è il nostro potenziostato/galvanostato di nuova generazione, con il nuovo software di Autolab INTELLO .

VIONIC offre la **combinazione di caratteristiche tecniche più versatile di qualsiasi altro strumento singolo** disponibile al momento sul mercato.

- Tensione conforme:  $\pm 50$  V
- Corrente standard  $\pm 6$  A
- Frequenza EIS: fino a 10 MHz
- Intervallo di campionatura fino a 1  $\mu$ s

Nel prezzo di VIONIC sono incluse anche funzioni che normalmente rappresenterebbero un costo aggiuntivo con la maggior parte degli altri strumenti quali ad esempio:

- Spettroscopia di impedenza elettrochimica (EIS)
- Modalità flottante selezionabile
- Secondo elettrodo di rilevamento (S2)
- Scansione analogica



### Spettrometro Raman portatile i-Raman Plus 532H

i-Raman<sup>®</sup> Plus 532H fa parte della nostra serie di spettrometri Raman portatili insignita di premi ed è dotata della nostra innovativa tecnologia spettrometrica intelligente. Questo spettrometro Raman portatile utilizza un sensore con array CCD ad elevata efficienza quantica, il raffreddamento termoelettrico e un intervallo dinamico elevato per garantire prestazioni eccezionali con il minimo rumore, anche in caso di tempi di integrazione che arrivano fino a 30 minuti. In questo modo è possibile misurare anche segnali Raman deboli.

Lo strumento i-Raman Plus 532H si caratterizza per la combinazione unica di ampia gamma spettrale ed elevata risoluzione con configurazioni che consentono di effettuare misure da  $65\text{ cm}^{-1}$  a  $3.400\text{ cm}^{-1}$ . La base piccola, la leggerezza e il consumo ridotto di energia permettono di eseguire analisi Raman dappertutto, a livello di ricerca. i-Raman Plus è dotato di sonda a fibra ottica per un campionamento facile ed è utilizzabile con un supporto per cuvette, un videomicroscopio, un tavolo scorrevole XYZ con supporto per sonda, nonché con il nostro software per l'analisi multivariata BWIQ<sup>®</sup> e il software per l'identificazione BWID<sup>®</sup>. Con lo strumento i-Raman Plus, avrete sempre una soluzione Raman ad alta precisione per l'analisi qualitativa e quantitativa.