



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).

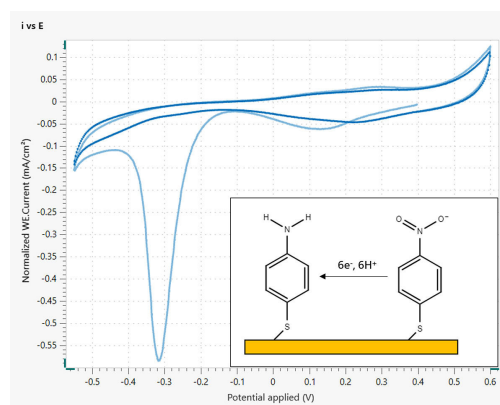


Figure 1. Cyclic voltammogram of 4-NTP adsorbed onto a roughened Au surface in 0.05 mol/L sulfuric acid.

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**.

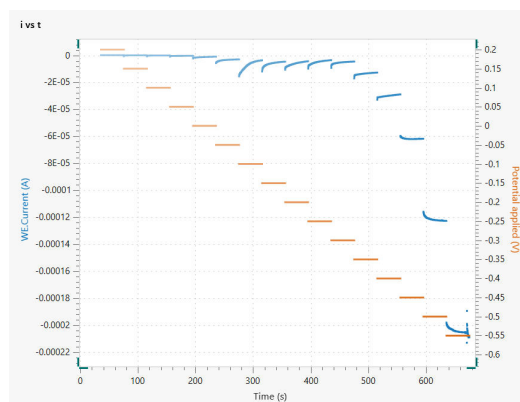


Figure 2. The electrochemical response of the 4-NTP monolayer recorded during the potential Step experiment in 0.05 mol/L sulfuric acid.

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

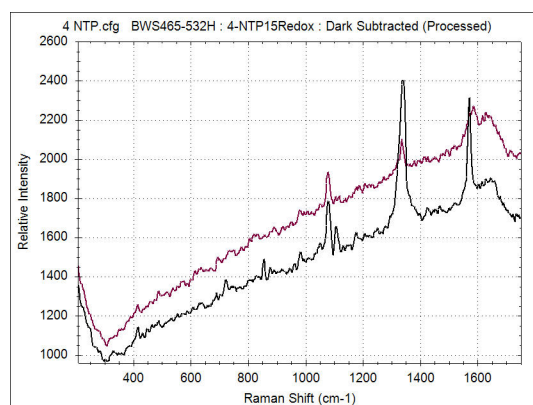


Figure 3. Raman spectra acquired at the first and last potential step during the potential step experiment (Figure 2).

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

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>.

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CONFIGURATION



VIONIC

VIONIC est notre potentiostat/galvanostat de dernière génération piloté par le nouveau logiciel d'Autolab, INTELLO.

VIONIC offre les **spécifications combinées les plus polyvalentes pour un appareil unique** actuellement sur le marché.

- Tension disponible : ± 50 V
- Intensité standard : ± 6 A
- Fréquence de SIE : jusqu'à 10 MHz
- Intervalle d'échantillonnage : jusqu'à 1 μ s

Le prix de VIONIC inclut également des fonctions qui impliquent généralement des coûts supplémentaires avec la plupart des autres appareils, telles que :

- Spectroscopie d'impédance électrochimique (SIE)
- Mode flottant sélectionnable
- Seconde électrode de détection (S2)
- Scan analogique



Spectromètre Raman portable i-Raman Plus 532H

L'i-Raman® Plus 532H appartient à notre série primée de spectromètres Raman portables « i-Raman », équipée de notre technologie de spectrométrie intelligente et innovante. Faisant appel à un détecteur à barrette CCD à haute efficacité quantique, avec refroidissement thermoélectrique et une gamme dynamique élevée, ce spectromètre Raman portable fournit des performances exceptionnelles avec un bruit réduit, même avec un temps d'intégration atteignant 30 minutes. Ainsi, les signaux Raman faibles peuvent aussi être mesurés.

Le i-Raman Plus 532H offre la combinaison exclusive d'une large gamme spectrale et d'une haute résolution avec des configurations autorisant des mesures de 65 cm^{-1} à $3\,400 \text{ cm}^{-1}$. Le faible encombrement et la légèreté de structure de ce système peu énergivore lui permettent d'effectuer partout des analyses Raman de qualité recherche. Équipé d'une sonde à fibre optique pour faciliter l'échantillonnage, l'i-Raman Plus peut être utilisé avec un support de cuvette, un microscope vidéo, une table de translation XYZ avec support de sonde ainsi qu'avec notre logiciel d'analyse à variantes multiples BWIQ® et le logiciel d'identification BWID®. Avec le i-Raman Plus, vous avez une solution Raman pérenne de haute fidélité pour l'analyse qualitative et quantitative.