



# Spectroelectrochemistry Applications Book

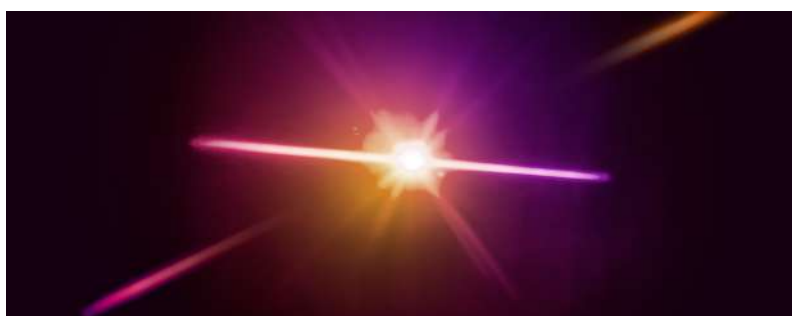
PEOPLE  
YOU  
CAN  
TRUST

 **Metrohm**  
DropSens

## Table of contents

Spectroelectrochemistry.....	1
UV-Vis spectroelectrochemistry.....	2
NIR spectroelectrochemistry.....	4
Raman spectroelectrochemistry.....	5
References.....	8

## *"Shedding light on the unknown"*



**Shedding light, in the literal sense of the phrase, on electrochemical knowledge and procedures. Spectroelectrochemistry offers analysts more information by being able to record both an optical and an electrochemical signal at the same time to obtain new data.**

The launch of the SPELEC systems represented an important breakthrough simplifying set-ups, facilitating data treatment and making the technique within everyone's reach.

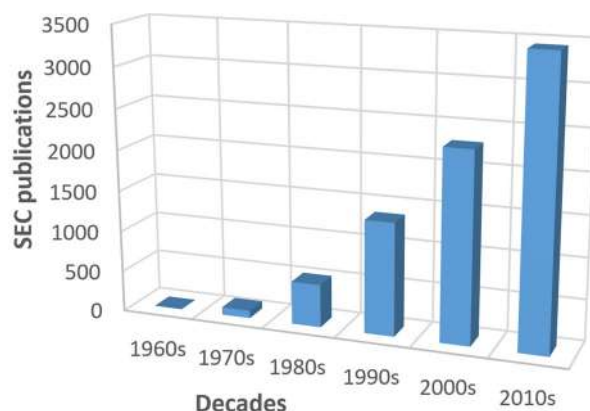
# Spectroelectrochemistry

**Spectroelectrochemistry (SEC) is a hybrid technique that joins the advantages of electrochemistry and spectroscopy<sup>1</sup>.**

This multi-response technique studies electrochemical reactions with the simultaneous optical monitorization of these processes. The acquisition of electrochemical and optical data gives an overview about the changes that take place on the electrode surface.

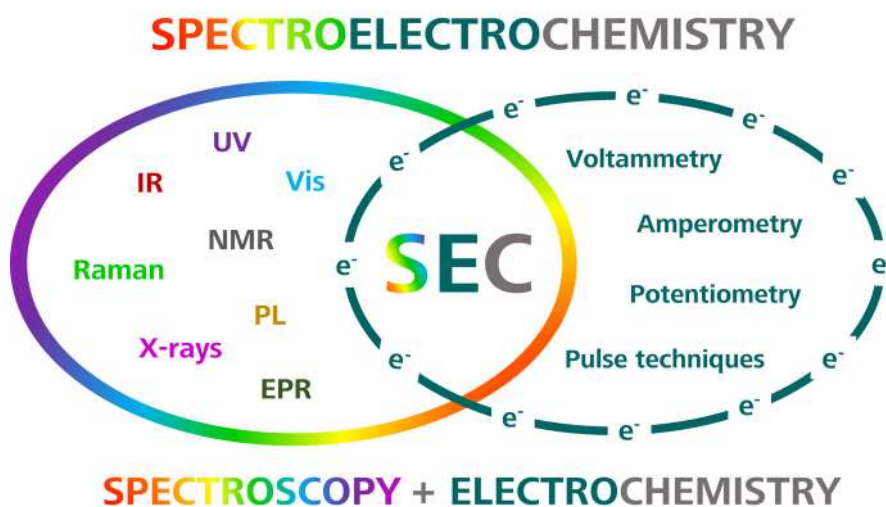
In a single experiment, spectroelectrochemistry provides two signals of different nature, being a very powerful feature to obtain valuable information about the studied system. However, the combination of electrochemical equipment (potentiostat/galvanostat) and spectroscopic instrumentation (light source and spectrometer) must ensure the perfect synchronization between electrochemical and optical signals.

Since the first work of spectroelectrochemistry was reported by Kuwana in 1964<sup>2</sup>, the number of works based on this technique have continuously grown, demonstrating the interest and its usefulness in different fields.



According to the spectral region, different information can be gathered from the spectroelectrochemical data. Each region of the electromagnetic spectrum is characterized by a range of frequencies or wavelengths and in that way, the characteristic energy related to each region provide specific information of the analyzed system.

Spectroelectrochemical features allow the development of new applications in different fields. In the following sections, the most relevant SEC applications are summarized. However, new ones are developed every day and they are not limited to those included in this document.



# UV-Vis spectroelectrochemistry

**Evolution of UV-Vis spectra (200-800 nm) simultaneously recorded with the electrochemical reaction displays molecular information related to the electronic levels of the molecules involved in the process.**

According to the final application, UV-Vis spectroelectrochemistry can be performed in different setup configurations:

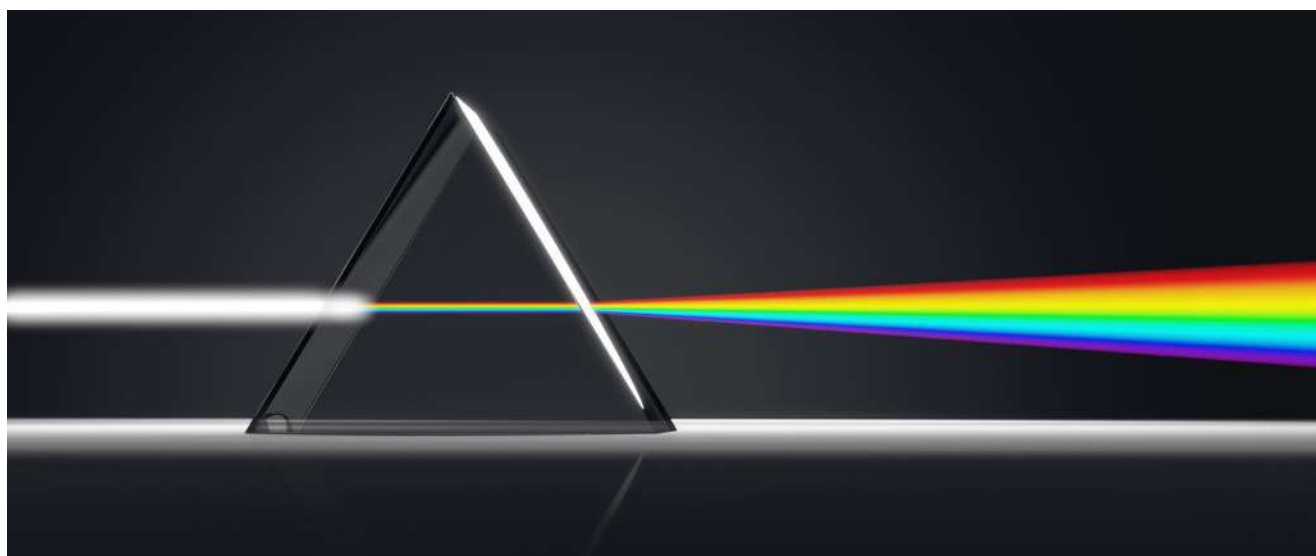
- Normal: the light beam samples the system perpendicularly to the electrode surface. It can be performed in two arrangements, reflection and transmission.
- Parallel: the light beam travels in parallel direction respect to the working electrode surface.
- Bidimensional: a perpendicular light beam and another one in parallel configuration are employed. Bidimensional can be defined as the simultaneous performance of normal and parallel spectroelectrochemistry.

Gathered information from UV-Vis spectroelectrochemistry is useful in the study of **reaction mechanisms** and in the assessing of electrochemical and optical parameters, but also **kinetic and thermodynamic information** of the analyzed process is obtained.

In that way, this multi-response technique is very useful in **fundamental chemistry**<sup>3,4</sup> as is demonstrated by the determination of absorptivity coefficients, standard potentials, diffusion coefficients, etc., but it is also an outstanding tool in **biomedical and life science**<sup>5-12</sup> for the characterization of process involving DNA, neurotransmitters, antitumor agents, etc., as well as in the monitorization of different **electrocatalytic processes**<sup>13-15</sup>.

However, the development of new spectroelectrochemical setups, cells and devices leads to the increase of applications in **material science**<sup>16-22</sup>, for instance, for the evaluation of shape, size, composition and distribution of nanostructures, or the complete characterization of organic and **inorganic compounds**<sup>23-26</sup>. Furthermore, different **energy devices**<sup>27,28</sup>, such as solar cells and rechargeable batteries as well as **environmental**<sup>29-31</sup> protocols are currently evaluated by UV-Vis spectroelectrochemistry.

According to the optical properties of UV-Vis spectroelectrochemistry, the use of this technique has been established in multiple and diverse applications. Among many others, Table 1 summarizes the most relevant application fields from top to bottom.



**Table 1**  
**Summary of the main applications of UV-Vis spectroelectrochemistry**  
**Spectral region: 200 - 800 nm**

Field	Application	System/Process
Fundamental chemistry	<ul style="list-style-type: none"> <li>- Elucidation of reaction mechanisms</li> <li>- Identification of intermediates</li> <li>- Quantification of generated products</li> <li>- Calculation of electrochemical and optical parameters</li> </ul>	<ul style="list-style-type: none"> <li>• Reversible and irreversible redox systems</li> </ul>
Biomedicine and life science	<ul style="list-style-type: none"> <li>- Monitoring of denaturation, renaturation, hybridization and interaction processes</li> <li>- Detection of biological compounds</li> <li>- Resolution of biological mixtures</li> </ul>	<ul style="list-style-type: none"> <li>• DNA</li> <li>• Neurotransmitters</li> <li>• Antioxidants</li> <li>• Antitumor agents</li> <li>• Proteins</li> <li>• Enzymes</li> </ul>
Electrocatalysis	<ul style="list-style-type: none"> <li>- Analysis of surface intermediates</li> <li>- Study of mechanism of electrodeposition of precursors</li> <li>- Monitoring of the stability and conversion of complexes</li> </ul>	<ul style="list-style-type: none"> <li>• Water oxidation reaction</li> <li>• Oxygen evolution</li> <li>• Hydrogen evolution</li> <li>• Transfer hydrogenation</li> </ul>
Material science	<ul style="list-style-type: none"> <li>- Characterization of morphological properties</li> <li>- Monitoring of doping processes</li> <li>- Determination of band-edge energies and the energy level offset</li> <li>- Ensuring electrogeneration processes</li> </ul>	<ul style="list-style-type: none"> <li>• Nanoparticles</li> <li>• Polymers</li> <li>• Perovskites</li> <li>• Quantum dots</li> <li>• Alloys</li> <li>• Composites</li> </ul>
Organic and inorganic chemistry	<ul style="list-style-type: none"> <li>- Study of the stability, degradation and redox-induced color changes</li> <li>- Understanding electronic coupling, charge delocalization, intraligand transitions and oxidation ligand-to-ligand charge transfer transitions.</li> </ul>	<ul style="list-style-type: none"> <li>• Organometallics</li> <li>• Coordination complexes</li> <li>• Phthalocyanines</li> <li>• Porphyrins</li> </ul>
Energy	<ul style="list-style-type: none"> <li>- Elucidation of the structure–property relationships</li> <li>- Analysis of the properties of oxidized and reduced forms</li> <li>- Study of the degree of charge delocalization</li> </ul>	<ul style="list-style-type: none"> <li>• Solar cells</li> <li>• Semiconductors</li> <li>• Rechargeable batteries</li> </ul>
Environmental	<ul style="list-style-type: none"> <li>- Monitoring of contaminants</li> <li>- Quantification of pollutants</li> <li>- Direct observation of amalgamations</li> </ul>	<ul style="list-style-type: none"> <li>• Filtration processes</li> <li>• Wastewaters</li> <li>• Mercury amalgamation</li> </ul>

## Just one software designed for spectroelectrochemistry



SPELEC instrument (UV-Vis range)

DropView SPELEC is a software thought and designed for (and by) those that want to treat spectroelectrochemical data in just one click.

DropView SPELEC is the only software in the market dedicated to spectroelectrochemistry.

For more info visit [www.metrohm-dropsens.com](http://www.metrohm-dropsens.com)

# NIR spectroelectrochemistry

**Spectroelectrochemistry in near-infrared region is associated with the vibrational energy of overtones and their combination of molecules that contain CH, NH and OH groups. It is concerned with absorption, emission, reflection, and diffuse-reflection of light in the region of 800-2500 nm.**

As spectroelectrochemistry in UV-Vis region, NIR spectroelectrochemical experiments can be performed in normal (reflection and transmission), parallel and bidimensional setup configuration.

Traditionally, the well-known high absorbance of water in this spectral range has limited the development of new applications of NIR spectroscopy.

However, this restriction is currently overcome using organic solvents and ionic liquids, but also

working in alternative configurations as thin-layer arrangement.

Particularly, the evaluation of the **electrochromic properties** is one of the most important applications of NIR spectroelectrochemistry in **material science**<sup>32-41</sup>. Furthermore, it is also an interesting tool for the elucidation of the electronic transitions of **organic and inorganic compounds**<sup>42,43</sup> and for the development of new protocols for **industrial applications**<sup>44</sup>.

Table 2 displays the main applications of NIR spectroelectrochemistry which have been developed according to the optical properties associated with this spectral range.

**Table 2**  
**Summary of the main applications of NIR spectroelectrochemistry**  
**Spectral region: 800 - 2500 nm**

Field	Application	System/Process
Material science	<ul style="list-style-type: none"><li>- Evaluation of electrochromic capabilities</li><li>- Modulation of optical properties</li><li>- Study of quantum confinements</li><li>- Monitoring of electrogeneration processes</li><li>- Analysis of switching of the doping state</li><li>- Study of the susceptibility to photoinduced electron transfer processes</li></ul>	<ul style="list-style-type: none"><li>• Electrochromic materials</li><li>• Semiconductors</li><li>• Nanocrystals</li><li>• Quantum dots</li><li>• Conducting polymers</li><li>• Carbon nanotubes</li></ul>
Organic and inorganic chemistry	<ul style="list-style-type: none"><li>- Unrevealing of electronic transitions</li><li>- Resolution of mixtures</li></ul>	<ul style="list-style-type: none"><li>• Coordination complexes</li><li>• Phthalocyanines</li><li>• Dyes</li></ul>



# Raman spectroelectrochemistry

**This spectroelectrochemical technique, based on the scattering of the incident light, has become an important tool in the study of electrochemical processes and in the characterization of many molecules. Its usefulness is clear since it provides specific information related to the structural changes, composition and orientation of the molecules involved in the electrochemical reaction.**

Raman spectroscopy is one of the most promising techniques for analysis due to its inherent fingerprint properties. In that way, it allows the identification and differentiation of species present in the system under study.

Although the traditional low sensitivity displayed by this technique has limited its use as detection method, surface-enhanced Raman scattering (SERS) effect has improved its analytical features. Thanks to the enhancement of the Raman signal, many sensing applications have been developed.

Raman spectroelectrochemical setup employs a laser as a monochromatic light source, being possible to work with different wavelengths depending on the final application.

The most used wavelengths are 532, 638 and 785 nm, being different the energy associated with each laser wavelength. At short wavelengths (more energy), the probability of damaging the sample as well as the generation of fluorescence during the measurement is increased. These two factors are usually taken into account for the selection of the adequate wavelength for each application.

## 532 nm laser

This wavelength is more energetic than 638 and 785 nm, so the risk of damage of the sample and the generation of fluorescence must be considered. 532 nm laser is traditionally focused on the characterization of **carbon materials**<sup>45-50</sup> due to their resonance Raman conditions.

This laser has been also used in the identification of **corrosion products**<sup>51</sup>, monitoring of electrochemical processes involved in **energy devices**<sup>52</sup>, and for the elucidation of **electrocatalytic reactions**<sup>53,54</sup>. The main applications of Raman spectroelectrochemistry using a 532 nm laser are included in Table 3.

**Table 3**  
**Summary of the main applications of Raman spectroelectrochemistry**  
**Laser waveleght: 532 nm**

Field	Application	System/Process
Material science	<ul style="list-style-type: none"><li>- Understanding redox behaviors</li><li>- Analysis of doping processes</li><li>- Evaluation of electron transfer capabilities and conductive properties</li><li>- Quantification of degradation processes</li><li>- Study of kinetics of degradation and oxidation states</li></ul>	<ul style="list-style-type: none"><li>• Carbon materials (single, double or multi-walled carbon nanotubes, graphene, fullerenes, etc.)</li><li>• Conducting polymers</li><li>• Composites and alloys</li></ul>
Corrosion	<ul style="list-style-type: none"><li>- Identification and monitoring of the transformation of products generated during corrosion processes</li></ul>	<ul style="list-style-type: none"><li>• Iron corrosion products</li></ul>
Energy	<ul style="list-style-type: none"><li>- Analysis of the intercalation of ions</li><li>- Evaluation of the disorder degree</li></ul>	<ul style="list-style-type: none"><li>• Graphite anodes</li></ul>
Electrocatalysis	<ul style="list-style-type: none"><li>- Elucidation of the structure and function of different catalysts</li></ul>	<ul style="list-style-type: none"><li>• Oxygen evolution reaction</li><li>• Hydrogen evolution reaction</li></ul>

## 638 nm laser

The energy provided by this wavelength ensures the balance between the risk of damaging the sample and the generation of fluorescence, making this laser often used for most **biological applications**<sup>55,56</sup>.

Moreover, this wavelength is useful for **sensing**<sup>57-59</sup> applications based on **SERS effect** and due to the resonance condition between the laser wavelength and the plasmon band of particular substrates. Many valuable information is also obtained in **electrocatalysis**<sup>60-62</sup>, achieving the understanding of essential processes.

Although the use of this wavelength is not as usual in **material science**<sup>63,64</sup>, it enables the elucidation of certain processes involved during electrochemical reactions. In a similar way, **corrosion studies**<sup>65</sup> on metallic electrodes have been carried out with 638 nm laser.

Table 4 summarizes the main applications of Raman spectroelectrochemistry using a 638 nm laser.

**SPELEC is the only instrumentation dedicated to spectroelectrochemistry where you will find in one system all components integrated and totally synchronized. Available in UV-Vis, NIR and Raman ranges**



SPELECRAMAN instrument

**Table 4**  
**Summary of the main applications of Raman spectroelectrochemistry**  
**Laser waveleght: 638 nm**

Field	Application	System/Process
Biology and life science	<ul style="list-style-type: none"> <li>- Determination of the copy number and relative distribution of mutations</li> <li>- Elucidation of oxidation mechanism of biological molecules</li> </ul>	<ul style="list-style-type: none"> <li>• Reversible and irreversible redox systems</li> </ul>
Sensing	<ul style="list-style-type: none"> <li>- Development of new detection methods based on SERS effect</li> <li>- SERS detection and quantification of chemical compounds</li> </ul>	<ul style="list-style-type: none"> <li>• DNA</li> <li>• Neurotransmitters</li> <li>• Antioxidants</li> <li>• Antitumor agents</li> <li>• Proteins</li> <li>• Enzymes</li> </ul>
Electrocatalysis	<ul style="list-style-type: none"> <li>- Analysis of the effect of certain molecules on oxidation/reduction processes</li> <li>- Monitoring of the electrocatalysis processes on specific surface sites of the catalyst</li> <li>- Acquisition of unambiguous evidences of the participation of different molecules on the reaction paths</li> </ul>	<ul style="list-style-type: none"> <li>• Oxidation of formic acid</li> <li>• Reduction of acetaldehyde oxime</li> <li>• Ammonia oxidation</li> </ul>
Material science	<ul style="list-style-type: none"> <li>- Ensuring the modification of the electrode surface</li> <li>- Monitoring of the doping and dedoping conversion</li> </ul>	<ul style="list-style-type: none"> <li>• Carbon nanotube composites</li> <li>• Conducting polymers</li> </ul>
Corrosion	<ul style="list-style-type: none"> <li>- Study of the inhibition of corrosion processes on metallic surfaces</li> </ul>	<ul style="list-style-type: none"> <li>• Iron electrodes</li> </ul>

## 785 nm laser

The energy associated with this wavelength reduces the fluorescence interference for most chemicals and provides excellent quality spectra. This laser is the most popular one for general applications of Raman spectroelectrochemistry and SERS studies due to its **exceptional versatility**.

For instance, the excellent properties shown by this technique facilitate the understanding of **fundamental processes**<sup>66,67</sup>.

The development of new **sensing platforms**<sup>68-80</sup> and protocols is highly related to SERS effect. The enhancement of Raman intensity allows the detection of **very low concentration of different analytes**.

At present, combination of Raman spectroscopy and electrochemistry is one of the most interesting techniques in the characterization of **materials**<sup>81-83</sup> due to the vibrational information gathered.

In addition, fingerprint properties are crucial in the monitorization of **electrocatalytic reactions**<sup>84-86</sup>, **energy devices**<sup>87-89</sup> and **corrosion processes**<sup>90</sup>. Furthermore, position and intensity of Raman bands but also their changes with potential is key point in the characterization of **organic and inorganic compounds**<sup>91</sup>.

Table 5 shows the most relevant applications based on Raman spectroelectrochemistry and SERS effect with 785 nm laser.



**Table 5**  
**Summary of the main applications of Raman spectroelectrochemistry**  
**Laser waveleght: 785 nm**

Field	Application	System/Process
Fundamental chemistry	<ul style="list-style-type: none"><li>- Monitoring of redox transformations</li><li>- Identification of intermediates and products</li><li>- Elucidation of reaction mechanisms</li></ul>	<ul style="list-style-type: none"><li>• Reversible and irreversible redox systems</li></ul>
Sensing	<ul style="list-style-type: none"><li>- Development of new detection methods based on SERS effect</li><li>- SERS detection and quantification of a huge variety of chemical compounds</li></ul>	<ul style="list-style-type: none"><li>• Drugs in pharma</li><li>• Xenobiotics in biological fluids</li><li>• Biomarkers in biological fluids</li><li>• Environmental and food contaminants</li></ul>
Material science	<ul style="list-style-type: none"><li>- Study of Fermi level and electronic states</li><li>- Monitoring of doping level changes</li></ul>	<ul style="list-style-type: none"><li>• Carbon materials</li><li>• Conducting polymers</li></ul>
Electrocatalysis	<ul style="list-style-type: none"><li>- Detection of metastable reaction intermediates</li><li>- Definition of complex reaction pathways</li><li>- Elucidation of reaction mechanisms</li></ul>	<ul style="list-style-type: none"><li>• Reduction of CO<sub>2</sub></li><li>• Oxygen reduction reaction</li></ul>
Energy	<ul style="list-style-type: none"><li>- Monitoring of switching processes between metastable states with different conductivity</li><li>- Identification of discharge products</li><li>- Understanding the evolution during discharge and charge cycling</li></ul>	<ul style="list-style-type: none"><li>• Solid-state polythiophene/viologen memory devices</li><li>• New materials for electrical energy storage</li><li>• Li-O<sub>2</sub> batteries</li></ul>
Corrosion	<ul style="list-style-type: none"><li>- Elucidation of the interactions and the reactions of different ions with metallic surfaces</li></ul>	<ul style="list-style-type: none"><li>• Corrosion inhibitor on copper surfaces</li></ul>
Organic and inorganic chemistry	<ul style="list-style-type: none"><li>- Investigation of vibrational characteristics</li><li>- Evaluation of charge-transfer mechanisms</li></ul>	<ul style="list-style-type: none"><li>• Organometallics</li><li>• Coordination compounds</li></ul>

# References

---

- (1) Kaim, W.; Fiedler, J. *Chem. Soc. Rev.* 2009, 38, 3373–3382.
- (2) Kuwana, T.; Darlington, R. K.; Leedy, D. W. *Anal. Chem.* 1964, 36, 2023–2025.
- (3) Heras, A.; Colina, A.; Ruiz, V.; López-Palacios, J. *Electroanalysis* 2003, 15, 702–708.
- (4) Zhangyu, Y.; Tiande, G.; Mei, Q. *Anal. Chem.* 1994, 66, 497–502.
- (5) Nowicka, A. M.; Zabost, E.; Donten, M.; Mazerska, Z.; Stojek, Z. *Bioelectrochemistry* 2007, 70, 440–445.
- (6) Syed, S. N.; Schulze, H.; MacDonald, D.; Crain, J.; Mount, A. R.; Bachmann, T. T. *J. Am. Chem. Soc.* 2013, 135, 5399–5407.
- (7) Gonzalez-Dieguez, N.; Colina, A.; Lopez-Palacios, J.; Heras, A. *Anal. Chem.* 2012, 84, 9146–9153.
- (8) He, J. B.; Yuan, S. J.; Du, J. Q.; Hu, X. R.; Wang, Y. *Bioelectrochemistry* 2009, 75, 110–116.
- (9) Nowicka, A. M.; Zabost, E.; Donten, M.; Mazerska, Z.; Stojek, Z. *Electroanalysis* 2007, 19, 214–219.
- (10) Olmo, F.; Garoz-Ruiz, J.; Colina, A.; Heras, A. *Anal. Bioanal. Chem.* 2020, 412, 6329–6339.
- (11) Zhao, X.; Nilges, M. J.; Lu, Y. *Biochemistry* 2005, 44, 6559–6564.
- (12) Vogt, S.; Schneider, M.; Schäfer-Eberwein, H.; Nöll, G. *Anal. Chem.* 2014, 86, 7530–7535.
- (13) Redman, D. W.; Rose, M. J.; Stevenson, K. J. *Langmuir* 2017, 33, 9354–9360.
- (14) Takashima, T.; Hashimoto, K.; Nakamura, R. J. *Am. Chem. Soc.* 2012, 134, 1519–1527.
- (15) McSkimming, A.; Chan, B.; Bhadbhade, M. M.; Ball, G. E.; Colbran, S. B. *Chem. - A Eur. J.* 2015, 21, 2821–2834.
- (16) Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P. *Nat. Mater.* 2008, 7, 442–453.
- (17) Fernandez-Blanco, C.; Heras, A.; Ruiz, V.; Colina, A. *RSC Adv.* 2014, 4, 45168–45173.
- (18) Izquierdo, D.; Martinez, A.; Heras, A.; Lopez-Palacios, J.; Ruiz, V.; Dryfe, R. A. W.; Colina, A. *Anal. Chem.* 2012, 84, 5723–5730.
- (19) Shallcross, R. C.; Zheng, Y.; Saavedra, S. S.; Armstrong, N. R. *J. Am. Chem. Soc.* 2017, 139, 4866–4878.
- (20) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M.; Reho, V. J. *Am. Chem. Soc.* 2008, 130, 6734–6736.
- (21) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* 1998, 31, 5051–5058.
- (22) Boehme, S. C.; Vanmaekelbergh, D.; Evers, W. H.; Siebbeles, L. D. A.; Houtepen, A. J. *J. Phys. Chem. B* 2016, 120, 5164–5173.
- (23) Tsai, C. H.; Chirdon, D. N.; Kagalwala, H. N.; Maurer, A. B.; Kaur, A.; Pintauer, T.; Bernhard, S.; et al. *Chem - A Eur. J.* 2015, 21, 11517–11524.
- (24) Ansari, M. A.; Mandal, A.; Paretzki, A.; Beyer, K.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* 2016, 55, 12357–12365.
- (25) Karaođlan, G. K.; Hıřır, A.; Maden, Y. E.; Karakuř, M. Ö.; Koca, A. *Dye. Pigment.* 2022, 204, 110390.
- (26) Dimé, A. K. D.; Catey, H.; Lucas, D.; Devillers, C. H. *J. Mol. Struct.* 2021, 1226, 129321.
- (27) Puodziukynaite, E.; Wang, L.; Schanze, K. S.; Papanikolas, J. M.; Reynolds, J. R. *Polym. Chem.* 2014, 5, 2363–2369.
- (28) Jiménez, P.; Levillain, E.; Alévêque, O.; Guyomard, D.; Lestriez, B.; Gaubicher, J. *Angew. Chemie - Int. Ed.* 2017, 56, 1553–1556.
- (29) Ibañez, D.; Gomez, E.; Valles, E.; Colina, A.; Heras, A. *Electrochim. Acta* 2018, 280, 17–24.
- (30) Prado, T. M.; Cincotto, F. H.; Machado, S. A. S. *Electrochim. Acta* 2017, 233, 105–112.
- (31) Schopf, C.; Wahl, A.; Martín, A.; O’Riordan, A.; Iacopino, D. J. *Phys. Chem. C* 2016, 120, 19295–19301.
- (32) Nie, G.; Wang, L.; Liu, C. J. *Mater. Chem. C* 2015, 3, 11318–11325.
- (33) Zheng, W.; Wang, B. B.; Lai, J. C.; Wan, C. Z.; Lu, X. R.; Li, C. H.; You, X. Z. *J. Mater. Chem. C* 2015, 3, 3072–3080.
- (34) Baran, D.; Balan, A.; Celebi, S.; Meana-Esteban, B.; Neugebauer, H.; Sariciftci, N. S.; Toppare, L. *Chem. Mater.* 2010, 22, 2978–2987.
- (35) Dahlman, C. J.; Leblanc, G.; Bergerud, A.; Staller, C.; Adair, J.; Milliron, D. J. *Nano Lett.* 2016, 16, 6021–6027.
- (36) Ou, W.; Zou, Y.; Wang, K.; Gong, W.; Pei, R.; Chen, L.; Pan, Z.; Fu, D.; Huang, X.; Zhao, Y.; et al. *J. Phys. Chem. Lett.* 2018, 9, 274–280.
- (37) Abd-Elwahed, A.; Holze, R. *Russ. J. Electrochem.* 2003, 39, 391–396.
- (38) Picard, L.; Lincker, F.; Kervella, Y.; Zagorska, M.; DeBettignies, R.; Peigney, A.; Flahaut, E.; Louarn, S.; et al. *J. Phys. Chem. C* 2009, 113, 17347–17354.
- (39) Jeong, K. S.; Deng, Z.; Keuleyan, S.; Liu, H.; Guyot-Sionnest, P. *J. Phys. Chem. Lett.* 2014, 5, 1139–1143.
- (40) Kavan, L.; Dunsch, L. *ChemPhysChem* 2003, 4, 944–950.
- (41) Oelsner, C.; Herrero, M. A.; Ehli, C.; Prato, M.; Guldi, D. M. *J. Am. Chem. Soc.* 2011, 133, 18696–18706.
- (42) Santos, J. J.; Ando, R. A.; Toma, S. H.; Corio, P.; Araki, K.; Toma, H. E. *Inorg. Chem.* 2015, 54, 9656–9663.
- (43) Dmitrieva, E.; Sturtz, B. W.; Yang, Y.; Zhang, P.; Dunsch, L.; Kenney, M. E. *Electrochem. Commun.* 2021, 128, 107048.
- (44) Ibáñez, D.; Pérez-Junquera, A.; González-García, M. B.; Hernández-Santos, D.; Fanjul-Bolado, P. *Phys. Chem. Chem. Phys.* 2019, 21, 6314–6318.
- (45) Mažeikienė, R.; Statino, A.; Kuodis, Z.; Niaura, G.; Malinauskas, A. *Electrochem. Commun.* 2006, 8, 1082–1086.
- (46) Mažeikienė, R.; Niaura, G.; Malinauskas, A. *J. Colloid Interface Sci.* 2009, 336, 195–199.

- (47) Mažeikienė, R.; Niaura, G.; Malinauskas, A. *Electrochim. Acta* 2008, 53, 7736–7743.
- (48) Ibañez, D.; Romero, E. C.; Heras, A.; Colina, A. *Electrochim. Acta* 2014, 129, 171–176.
- (49) Kim, Y. A.; Kojima, M.; Muramatsu, H.; Umemoto, S.; Watanabe, T.; Yoshida, K.; Sato, K.; Ikeda, T.; Hayashi, T.; Endo, M.; et al. *Small* 2006, 2, 667–676.
- (50) Kalbac, M.; Farhat, H.; Kong, J.; Janda, P.; Kavan, L.; Dresselhaus, M. S. *Nano Lett.* 2011, 11, 1957–1963.
- (51) Genchev, G.; Erbe, A. J. *Electrochem. Soc.* 2016, 163, C333–C338.
- (52) Shimizu, M.; Koya, T.; Nakahigashi, A.; Urakami, N.; Yamakami, T.; Arai, S. *J. Phys. Chem. C* 2020, 124, 13008–13016.
- (53) Kornienko, N.; Resasco, J.; Becknell, N.; Jiang, C. M.; Liu, Y. S.; Nie, K.; Sun, X.; Guo, J.; Leone, S. R.; Yang, P. J. *Am. Chem. Soc.* 2015, 137, 7448–7455.
- (54) Rivera-Gavidia, L. M.; Luis-Sunga, M.; Bousa, M.; Vales, V.; Kalbac, M.; Arévalo, M. C.; Pastor, E.; García, G. *Electrochim. Acta* 2020, 340, 135975.
- (55) Mahajan, S.; Richardson, J.; Gaied, N. Ben; Zhao, Z.; Brown, T.; Bartlett, P. N. *Electroanalysis* 2009, 21, 2190–2197.
- (56) Ibañez, D.; Santidrian, A.; Heras, A.; Kalbáč, M.; Colina, A. J. *J. Phys. Chem. C* 2015, 119, 8191–8198.
- (57) Hernandez, S.; Garcia, L.; Perez-Estebanez, M.; Cheuquepan, W.; Heras, A.; Colina, A. J. *Electroanal. Chem.* 2022, 918, 116478.
- (58) Abdelsalam, M.; Bartlett, P. N.; Russell, A. E.; Baumberg, J. J.; Calvo, E. J.; Tognalli, N. G.; Fainstein, A. *Langmuir* 2008, 24, 7018–7023.
- (59) Abdelsalam, M. E.; Mahajan, S.; Bartlett, P. N.; Baumberg, J. J.; Russell, A. E. J. *Am. Chem. Soc.* 2007, 129, 7399–7406.
- (60) Solla-Gullón, J.; Vidal-Iglesias, F. J.; Pérez, J. M.; Aldaz, A. *Electrochim. Acta* 2009, 54, 6971–6977.
- (61) Vidal-Iglesias, F. J.; Solla-Gullón, J.; Orts, J. M.; Rodes, A.; Pérez, J. M.; Feliu, J. M. J. *J. Phys. Chem. C* 2012, 116, 10781–10789.
- (62) Vidal-Iglesias, F. J.; Solla-Gullón, J.; Pérez, J. M.; Aldaz, A. *Electrochem. commun.* 2006, 8, 102–106.
- (63) Tsai, M. H.; Lin, Y. K.; Luo, S. C. *ACS Appl. Mater. Interfaces* 2019, 11, 1402–1410.
- (64) Pelto, J.; Haimi, S.; Puukilainen, E.; Whitten, P. G.; Spinks, G. M.; et al. *Biomed. Mater. Res. - Part A* 2010, 93, 1056–1067.
- (65) Yao, J. L.; Ren, B.; Huang, Z. F.; Cao, P. G.; Gu, R. A.; Tian, Z. Q. *Electrochim. Acta* 2003, 48, 1263–1271.
- (66) Hernandez, S.; Perales-Rondon, J. V.; Heras, A.; Colina, A. *Nano Res.* 2022, 15, 5340–5346.
- (67) Mažeikienė, R.; Niaura, G.; Malinauskas, A. J. *Electroanal. Chem.* 2011, 660, 140–146.
- (68) Zaleski, S.; Clark, K. A.; Smith, M. M.; Eilert, J. Y.; Doty, M.; Van Duyne, R. P. *Anal. Chem.* 2017, 89, 2497–2504.
- (69) Hernandez, S.; Perales-Rondon, J. V.; Heras, A.; Colina, A. *Electrochim. Acta* 2020, 334, 135561.
- (70) González-Hdez, J.; Ott, C. E.; Arcos-Martínez, M. J.; Colina, A.; Heras, A.; Alvarado-Gómez, A. L.; Urcuyo, R.; Arroyo-Mora, L. E. *Sensors* 2021, 22, 295.
- (71) Sanger, K.; Durucan, O.; Wu, K.; Thilsted, A. H.; Heiskanen, A.; Rindzevicius, T.; Schmidt, M. S.; Zór, K.; Boisen, A. *ACS Sensors* 2017, 2, 1869–1875.
- (72) Greene, B. H. C.; Alhatab, D. S.; Pye, C. C.; Brosseau, C. L. *J. Phys. Chem. C* 2017, 121, 8084–8090.
- (73) Bindesri, S. D.; Jebailey, R.; Albarghouthi, N.; Pye, C. C.; Brosseau, C. L. *Analyst* 2020, 145, 1849–1857.
- (74) Karaballi, R. A.; Nel, A.; Krishnan, S.; Blackburn, J.; Brosseau, C. L. *Phys. Chem. Chem. Phys.* 2015, 17, 21356–21363.
- (75) Mohammadniaei, M.; Yoon, J.; Lee, T.; Choi, J. W. *J. Biotechnol.* 2018, 274, 40–46.
- (76) Hernandez, S.; Perales-Rondon, J. V.; Heras, A.; Colina, A. *Anal. Chim. Acta* 2019, 1085, 61–67.
- (77) Hassanain, W. A.; Izake, E. L.; Ayoko, G. A. *Anal. Chem.* 2018, 90, 10843–10850.
- (78) Sarfo, D. K.; Izake, E. L.; O'Mullane, A. P.; Wang, T.; Wang, H.; Tesfamichael, T.; Ayoko, G. A. *Sensors Actuators, B Chem.* 2019, 287, 9–17.
- (79) Ibañez, D.; González-García, M. B.; Fanjul-Bolado, et al. *P. Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 2021, 248, 119174–119180.
- (80) Bindesri, S. D.; Alhatab, D. S.; Brosseau, C. L. *Analyst* 2018, 143, 4128–4135.
- (81) Takeda, N.; Murakoshi, K. *Anal. Bioanal. Chem.* 2007, 388, 103–108.
- (82) Okazaki, K.; Nakato, Y.; Murakoshi, K. *Phys. Rev. B* 2003, 68, 035434.
- (83) Liu, C.; Zhang, J.; Shi, G.; Chen, F. *J. Appl. Polym. Sci.* 2004, 92, 171–177.
- (84) Moradzaman, M.; Mul, G. *ChemElectroChem* 2021, 8, 1478–1485.
- (85) An, A. H.; Wu, L.; Mandemaker, L.; Ruiters, J. De; Wijten, J.; Janssens, J.; Stam, W.; et al. *Angew. Chemie - Int. Ed.* 2021, 60, 16576–16584.
- (86) Yu, H. Y.; Li, X. F.; Zhang, T. H.; Liu, J.; Tian, J. H.; Yang, R. *ChemSusChem* 2020, 13, 2702–2708.
- (87) Kumar, R.; Pillai, R. G.; Pekas, N.; Wu, Y.; McCreery, R. L. *J. Am. Chem. Soc.* 2012, 134, 14869–14876.
- (88) Gittleston, F. S.; Ryu, W. H.; Taylor, A. D. *ACS Appl. Mater. Interfaces* 2014, 6, 19017–19025.
- (89) Rodríguez-Calero, G. G.; Conte, S.; Lowe, M. A.; Burkhardt, S. E.; Gao, J.; John, J.; et al. *J. Electroanal. Chem.* 2016, 765, 65–72.
- (90) Hurley, B. L.; McCreery, R. L. *J. Electrochem. Soc.* 2003, 150, B367–B373.
- (91) López-Tocón, I.; Imbarack, E.; Soto, J.; Sanchez-Cortes, S.; Leyton, P.; Otero, J. C. *Molecules* 2019, 24, 4622.



### **Further information**

Please contact your Metrohm representative or  
Metrohm DropSens at [info.dropsens@metrohm.com](mailto:info.dropsens@metrohm.com)

#### **Metrohm DropSens S.L.**

Vivero Ciencias de la Salud  
C/ Colegio Santo Domingo de Guzmán s/n  
33010 Oviedo, Spain  
[www.metrohm-dropsens.com](http://www.metrohm-dropsens.com)

