

Editorial

Polymer-Based Chemical Sensors

José Antonio Reglero Ruiz *, Saúl Vallejos, Félix Clemente García and José Miguel García *

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain; svallejos@ubu.es (S.V.); fegarcia@ubu.es (F.C.G.)

* Correspondence: jareglero@ubu.es (J.A.R.R.); jmiguel@ubu.es (J.M.G.); Tel.: +34-947-25-80-85 (J.A.R.R.)

Received: 18 September 2018; Accepted: 19 September 2018; Published: 19 September 2018



1. Introduction

The development of supramolecular chemistry by Pedersen, Cram, and Lehn in the 1960s brought forth the growth of a new research field called chemical sensors or chemosensors. These are molecules having receptor or host units devoted to providing information about the chemical composition of its environment through selective interaction with target molecules (guest molecules). The chemical sensors are usually organic or organometallic low-mass molecules with a number of drawbacks: They are generally water insoluble, exhibit moderate to low light and thermal stability, and tend to migrate when they are dispersed in physical supports.

Polymer-based chemistry has led to a completely new family of sensory materials and devices employing polymers which present the ability to show a response when they are in contact with a target species. The selective interaction that gives rise to the response relay on the recognition of the target species, or guest analyte, by the receptor motifs of the polymer, and it must be followed by a transduction process originating an easily measurable change [1–3]. In addition, polymeric sensors can be easily manufactured into different shapes such as micro/fibers, films, beads, coatings, wires, etc. For this reason, they are currently used in many applications [4–7].

Although the number of polymeric materials with sensory properties are continuously evolving, we can highlight, for example, molecularly imprinted polymers, polymeric nanocomposites and hybrid polymers, acrylic polymers, conjugated or conductive polymers, polymers with chiral motifs or sensor arrays based on a set of polymers [8–12].

In parallel, the number of target analytes which can be detected and quantified has grown exponentially. We can point out, for example, the detection of metallic cations and anions [13], gases and volatile organic compounds (VOCs) [14], a fundamental research line devoted to the detection of explosives and chemical warfare agents [15,16] and the detection of target species in new and interesting biological and biomedical applications [17,18].

2. The Special Issue

This special issue is focused in the last advancements of polymer-based chemical sensors, offering a very interesting platform in which the last developments in the quick-evolving field of polymeric sensors can be found. A total number of seven contributions show the main research lines, pointing out future perspectives and also the associated problems to overcome in the next years. We proceed now to describe the main results derived from these research works.

Petrov et al. [19] present different theoretical studies of the interaction of molecules of several gaseous pollutants with polyacrylonitrile (PAN) surface in the presence of a water and/or oxygen molecule, using quantum chemical calculations and molecular modeling. The results conclude that PAN in atmospheric air in the presence of oxygen molecules is sensitive to different target species, such as carbon oxide (IV), sulfur (IV) oxide, chlorine, hydrogen sulfide and carbon oxide (II). Also,

it was observed that, theoretically, the presence of water molecules in the polluted atmosphere does not affect the gas sensitivity of PAN films.

The second contribution is presented by Ali et al. [20]. The work investigates the possible chemical changes in polydimethylsiloxane (PDMS) caused by two different techniques of fabrication for ultra-sensitive electric field optical sensors. The authors developed an optical sensing device consisting in a micro-sphere made from 60:1 PDMS (60 parts base silicon elastomer to one part polymer curing agent by volume), performing detection measurements based on the morphology-dependent resonances (MDR) shifts of the micro-sphere, analyzing also the influence of curing and poling of polymer micro-spheres used as optical sensors.

Ziegler et al. [21] describe biochar-based humidity sensors, prepared by drop-coating technique. Polyvinylpyrrolidone (PVP) was employed as an organic binder to improve the adhesion of the sensing material onto ceramic substrates having platinum electrodes. The performance of the sensory devices is tested at varying relative humidities (RH) at room temperature, showing variations up to two orders of magnitude in the measured impedance. Also, the authors present a reasonably fast response and recovery times (in the order of 1 min).

The fourth contribution is presented by Sachan et al. [22], studying nanocomposite-based quantum resistive vapour sensors (vQRS), developed from the assembly of hybrid copolymers of polyhedral oligomeric silsesquioxane (POSS) and poly(methyl methacrylate) (PMMA) or poly(styrene) (PS) with carbon nanotubes (CNT). These novel transducers are employed to detect sub-ppm concentrations of ammonia and formaldehyde at room temperature despite the presence of humidity. Detection limits values are around 300 ppb of formaldehyde and 500 ppb of ammonia with a sufficiently good signal to noise ratio ($SNR > 10$) and quick response times (below 5 s). These devices could be potentially used in applications of POSS-based vQRS for air quality or volatolome monitoring, for example.

Reglero Ruiz et al. [23] present a complete review listing the most recent developments concerning the application of sensory polymers in the detection and quantification of different target species. The review describes the main polymers employed as sensory polymers, including, for example, conducting polymers, acrylate-based polymers and polymer nanocomposites, the different mechanisms of detection and the target species, such as metal cations and anions, explosives, and biological and biomedical substances, ending with the advancements concerning the fabrication of micro and nano sensory devices based on smart polymers.

Si et al. [24] describe the monitoring of the concentrations of various neurotransmitters, which are of great importance in studying and diagnosing serious mental disorders such as Parkinson's disease, schizophrenia, and Alzheimer's disease. The review is focused in different aspects of this research field. First, the analysis of the common materials used for developing neurotransmitter sensors is discussed. Secondly, several sensor surface modification approaches to enhance sensing performance are reviewed. To conclude, the recent developments in the simultaneous detection capability of multiple neurotransmitters is presented. The review also remarks the main challenges for in vivo electrochemical neurotransmitter sensors, which are their limited target selectivity, large background signal and noise, and device fouling and degradation over time.

The last contribution to the Special Issue is presented by Cinti. [25] The author presents the last advances in design of selective interfaces and printed technology, which led to the improvement of the electro analysis detection methods. In this sense, the main advantage in electroanalytical field is the possibility to manufacture and customize plenty of different sensing platforms, thus avoiding expensive equipment, hiring skilled personnel, and expending economic effort. The review provides an overview of the technical procedures that are used in order to establish polymer effectiveness in printed-based electroanalytical methods, pointing out special attention to the development of electroanalytical sensors and biosensors, in which the role of polymer-based materials is becoming essential.

The contributions published in this Special Issue collect key information combined to the last advancements in this quick evolving research field, providing both the key ideas and recent

applications of polymer-based chemical sensors, and we hope that they will be of great interest to the readers of *Chemosensors*.

Acknowledgments: We would like to thank all authors who contributed with their excellent papers to this Special Issue (SI). We thank the anonymous reviewers for their fundamental help in assuring the high quality of the SI. We are grateful to the *Chemosensors* Editorial Office for giving us the opportunity and, in particular, to Lilian Liu for her continuous support in managing and organizing this SI.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cichosz, S.; Masek, M.; Zaborski, M. Polymer-based sensors: A review. *Polym. Test.* **2018**, *67*, 342–348. [[CrossRef](#)]
2. García, J.M.; García, F.C.; Serna, F.; de la Peña, J.L. Fluorogenic and chromogenic polymer chemosensors. *Polym. Rev.* **2011**, *51*, 341–390. [[CrossRef](#)]
3. García, J.M.; Pablos, J.L.; García, F.C.; Serna, F. Sensory polymers for detecting explosives and chemical warfare agents. In *Industrial Applications for Intelligent Polymers and Coatings*, 1st ed.; Hosseini, M., Makhoulouf, A.S., Eds.; Springer International Publishing: Cham, Switzerland, 2016; pp. 553–576. ISBN 978-3-319-26893-4.
4. Jeong, B.; Gutowska, A. Lessons from nature: Stimuli-responsive polymers and their biomedical applications. *Trends Biotechnol.* **2002**, *20*, 305–311. [[CrossRef](#)]
5. Bajpai, A.K.; Sandeep, K.S.; Bhanu, S.; Kankane, S. Responsive polymers in controlled drug delivery. *Prog. Polym. Sci.* **2008**, *33*, 1088–1118. [[CrossRef](#)]
6. Balint, R.; Cassidy, N.; Cartmell, S. Conductive polymers: Towards a smart biomaterial for tissue engineering. *Acta Biomater.* **2014**, *10*, 2341–2353. [[CrossRef](#)] [[PubMed](#)]
7. Hu, J.; Liu, S. Responsive polymers for detection and sensing applications: current status and future developments. *Macromolecules* **2010**, *43*, 8315–8330. [[CrossRef](#)]
8. Uzun, L.; Turner, A.P. Molecularly-imprinted polymer sensors: Realizing their potential. *Biosens. Bioelectron.* **2016**, *76*, 131–144. [[CrossRef](#)] [[PubMed](#)]
9. Jordan, J.; Jacob, K.L.; Tannenbaum, R.; Sharaf, M.A.; Jasiuk, I. Experimental trends in polymer nanocomposites—A review. *Mater. Sci. Eng. A* **2005**, *393*, 1–11. [[CrossRef](#)]
10. Saunders, K.J. Acrylic polymers. In *Organic Polymer Chemistry*, 2nd ed.; Springer: Dodrecht, Germany, 1988; pp. 125–148. ISBN 978-94-009-1195-6.
11. MacDiarmid, A.G.; Mammone, R.J.; Kaner, R.B.; Porter, S.J. The concept of ‘doping’ of conducting polymers: The role of reduction potentials. *Philos. Trans. R. Soc. A* **1985**, *314*, 3–15. [[CrossRef](#)]
12. Okamoto, Y. Chiral polymers. *Prog. Polym. Sci.* **2000**, *25*, 159–162. [[CrossRef](#)]
13. Vallejos, S.; Estévez, P.; Ibeas, S.; Muñoz, A.; García, F.C.; Serna, F.; García, J.M. A selective and highly sensitive fluorescent probe of Hg²⁺ in organic and aqueous media: The role of a polymer network in extending the sensing phenomena to water environments. *Sens. Actuators B Chem.* **2011**, *157*, 686–690. [[CrossRef](#)]
14. Kwan, P.H.; MacLachlan, M.J.; Swager, T.M. Rotaxaned conjugated sensory polymers. *J. Am. Chem. Soc.* **2004**, *126*, 8638–8639. [[CrossRef](#)] [[PubMed](#)]
15. Pablos, J.L.; Trigo-López, M.; Serna, F.; García, F.C.; García, J.M. Solid polymer substrates and smart fibres for the selective visual detection of TNT both in vapor and in aqueous media. *RSC Adv.* **2014**, *4*, 25562–25568. [[CrossRef](#)]
16. Wang, E.; Sun, D.; Li, H.; Sun, X.; Liu, J.; Ren, Z.; Yan, S. High efficiency organosilicon-containing polymer sensors for the detection of trinitrotoluene and dinitrotoluene. *J. Mater. Chem. C* **2016**, *4*, 6756–6760. [[CrossRef](#)]
17. Eo, S.H.; Song, S.; Yoon, B.; Kim, J.M. A microfluidic conjugated-polymer sensor chip. *Adv. Mater.* **2008**, *20*, 1690–1694. [[CrossRef](#)]
18. Barone, P.W.; Yoon, H.; Ortiz-García, R.; Zhang, J.; Ahan, J.H.; Kim, J.H.; Strano, M.S. Modulation of single-walled carbon nanotube photoluminescence by hydrogel swelling. *ACS Nano* **2009**, *3*, 3869–3877. [[CrossRef](#)] [[PubMed](#)]

19. Petrov, V.; Avilova, M. Theoretical investigations of the interaction of gaseous pollutants molecules with the polyacrylonitrile surface. *Chemosensors* **2018**, *6*, 39. [[CrossRef](#)]
20. Ali, A.R.; Tourky, A.S.; Roushdy, A.A. Effect of dangling bonds on de-poling time for polymeric electric field optical sensors. *Chemosensors* **2018**, *6*, 3. [[CrossRef](#)]
21. Ziegler, D.; Palmero, P.; Giorcelli, M.; Tagliaferro, A.; Tulliani, J.-M. Biochars as innovative humidity sensing materials. *Chemosensors* **2017**, *5*, 35. [[CrossRef](#)]
22. Sachan, A.; Castro, M.; Choudhary, V.; Feller, J.-F. vQRS based on hybrids of CNT with PMMA-POSS and PS-POSS Copolymers to reach the sub-PPM detection of ammonia and formaldehyde at room temperature despite moisture. *Chemosensors* **2017**, *5*, 22. [[CrossRef](#)]
23. Reglero Ruiz, J.A.; Sanjuán, A.M.; Vallejos, S.; García, F.C.; García, J.M. Smart polymers in micro and nano sensory devices. *Chemosensors* **2018**, *6*, 12. [[CrossRef](#)]
24. Si, B.; Song, E. Recent advances in the detection of neurotransmitters. *Chemosensors* **2018**, *6*, 1. [[CrossRef](#)]
25. Cinti, S. Polymeric materials for printed-based electroanalytical (Bio)applications. *Chemosensors* **2017**, *5*, 31. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).