Nanomaterials properties tuned by their environment: integrating supramolecular concepts into sensing devices

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Self-organization and self-assembly enabled the development of hierarchically-organized (multi)functional materials through the subtle control of adaptive interactions between suitably designed building blocks. The use of non-covalent interactions to construct sophisticated supramolecular architectures makes it possible to transduce the modifications of their environment into precise modulation of their self-assembly behavior. The changes of properties upon small environmental variations can be enhanced or amplified through engineered assemblies integrated into devices. To cast an example, once the supramolecular interactions between a designed receptor and an analyte (for instance, a small molecule or an ion) present in the environment are efficiently coupled to the active area of a device, then extremely sensitive and selective sensors can be fabricated. The transducer readout can be either a change of mass, of optical properties (e.g. a modification of absorbance and/or fluorescence intensity), or a variation of parameters in electric characteristics (like a change of capacitance, transconductance, threshold voltage).

Supramolecular recognition can, therefore be the key-concept for the design and making of the next generation of sensors exhibiting detection limits down to sub-ppb level with fast response speed combined with unprecedented selectivity. These characteristics are the result of optimally designed non-covalent interactions through the integration of receptor groups possessing ad-hoc characteristics by design including size, geometry, dipole and quadrupole moments, surface charges, H- or halogen bonds. Since specific sensing is triggered by molecular recognition, the sensitivity can be harnessed by using low-dimensional structures exhibiting a high accessible surface area, decorated with receptors. These concepts can lead to devise the last generation of ultrasensitive and ultrasensitive sensors for food safety, environmental and biohealth monitoring, as well as for chemical- and biodefense.

This special issue focusses on the development of novel materials and their integration in sensing device to detect the presence of ions, heavy metals, small molecules and biomolecules. Such an environmental monitoring, which is also relevant to defense, security and safety applications, will unquestionably contribute to the improvement of people’s quality of life and will offer solutions even to some key biomedical questions such as early diagnostics and continuous monitoring of diseases.

In this context, metal organic frameworks (MOFs), when suitably engineered, can operate as highly sensitive and selective sensors. Shustova and co-workers describe the possibility of using optical readout by taking full advantage of the MOF’s light-harvesting ability, thereby opening intriguing perspectives in photocatalysis; Li and collaborators discussed the tailoring of such unique porous materials in order to efficiently capture toxic and hazardous gases and vapours.

Another family of materials particularly apt for sensing is the one of 2D materials, as these nanosystems feature a highest surfaces-to-volume ratio and exceptional opto-electronic properties which are highly sensitive to changes in the environment. Samori and co-workers showed that surface functionalization of graphene and molybdenum dichalcogenides with receptors of specific analytes makes it possible the development of highly sensitive and selective sensors for the detection of gases, ions and small biomolecules.

Among the various receptors, those based on macrocyclic compounds such as cyclodextrin, calixarenes, cucurbiturils and cucavands are surely the most reliable in terms of selectivity. Their application for biochemical sensors is reviewed by Dalcanale et al.

The quantitative identification of biomarkers is key for the early diagnostics of diseases. A powerful method, which is reviewed by Kotov, Liz-Marzan, Xu and co-workers consists in the in vitro and in vivo use of the plasmonic effect in functionalized metal nanoparticles. Towards the monitoring of the health of the world’s population, Merkoçi and colleagues discussed the use of different nanomaterials towards applications in point-of-care (PoC) diagnostic, a strategy that holds great potential for the development of miniaturized devices.

A novel approach towards biosensing, described by Lanzani, Benfenati and co-workers, relies in the development of artificial light actuators based on (in)organic semiconductors to transduce a light signal into a signal which affects biological activities livings systems, to ultimately control neural path and other vital functions.
Finally, the medical evaluation of potential diseases in a non-invasive manner has a paramount importance for the early diagnosis. Haick and collaborators describe how this can be accomplished via the analysis of volatile organic compounds (VOC) exhaled from breath, in combination with the analysis of human bodily fluids.

Chemical sensing is increasingly becoming less heuristic and more based on solid physico-chemical grounds. The chemistry approach to sensing is a fast expanding field of science which can take great advantage in the years to come from a rational design of functional low dimensional nanostructures whose properties are extremely sensitive to changes in the environment, in combination with the coupling to supramolecular receptors which are designed and synthesized from molecular biology or other emerging biotechnologies. We believe that this special issue will provide the readers with clear evidence and stimulating examples of the breadth of this field and possibly convey the enthusiasm of those scientists involved in this research. We are grateful to all of them for their effort in highlighting the fundamentals, the application and in several instances also the hurdles, subtleties and burning questions of the multidisciplinary field of chemical sensing.

**Biosketch**

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His research interests encompass supramolecular sciences, nanochemistry and materials chemistry with a specific focus on graphene and other 2D materials as well as functional organic/polymeric and hybrid nanomaterials for application in opto-electronics, energy and sensing. His work has been awarded various prizes, including the Young Scientist Award by E-MRS (1998) and MRS (2000), the IUPAC Prize for Young Chemists (2001), the ERC Starting Grant (2010), the CNRS Silver Medal (2012), the Spanish-French “Catalán-Sabatier” Prize (2017), the German-French “Georg Wittig - Victor Grignard” Prize (2017), the Surface and Interfaces Award by the RSC (2018) and the Blaise Pascal Medal in Materials Science by EURASC (2018).

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