

Editorial

Photonics and Plasmonics: New Challenges for Optical Nanostructured Materials in Sensing

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In the last decade, new technologies have undertaken an extraordinary development, based not only on new materials and new processes but also on design, modelling, information technology, and artificial intelligence. This Special Issue, which after the success of the issue has led to a second edition on similar topics, fits into this context of broad development and offers an updated overview in the field of chemical sensors and new intelligent materials. In fact, these enhanced materials bring together the benefits of many different components promoting in many cases properties and synergistic effects in the field of photonic and plasmonic sensors and biosensors. All this engenders a very effective mode of study and research which supplies substrates and suggestions for industrial needs and applications, ranging from biotechnology and optoelectronics to sensors, while also paying attention to the environmental impact of the processes and technologies described herein. This Special Issue aims to present the advancement of new plasmonic materials, their formulation, functionalization, characterization, and intelligent application in advanced fields, both through point works and reviews.

Kurniawan et al. [1] in their review, highlight the attractive properties and synthesis procedures of graphene quantum dots (GQDs). New developments in the production of GQD nanocomposites based on both organic and inorganic materials, and their optical properties, such as luminescence and surface-enhanced Raman scattering (SERS-based biosensing applications) are presented. The challenges and prospects in this research area are highlighted in the conclusion of this review.

In the work of Serafinelli et al. [2] the authors provide an overview of 2D nanomaterials and their properties. They also present the physical explanation of the typical phenomenon of surface plasmon resonance and localized surface plasmon resonance. Then, examples of hybrid nanomaterials that function as colorimetric biosensors are provided. To conclude, the authors' views on the actual status, challenges, and future objectives in plasmonic sensing and biosensing are provided. These authors also highlight the key role that these smart materials and new technologies can play in enhancing digitization and virtualization, including in pandemic management.

Moreover, stimulated by the amazing optical properties of plasmonic sensors, such as surface plasmon resonance (SPR), localized surface plasmon resonance (LSPR), SERS, and their ultra-sensitivity, single particle/molecular level detection capability, room temperature operation, and ease of miniaturization, numerous plasmonic sensors for the detection of lung cancer biomarkers have been also examined. In the review of Usman et al. [3] the theory behind the plasmonic sensor is described. Furthermore, new approaches and variations assumed for the finding of lung cancer biomarkers such as miRNA, carcinoembryonic antigen (CEA), cytokeratin, and volatile organic compounds (VOCs), are presented.



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Colombelli et al. [4] in their article, show how there are fascinating relationships between the geometry of various types of nanostructures and specific optical properties such as enhanced absorption or extraordinary transmission. In view of the use of such nanomaterials as optical sensors, these properties are studied and optimized together with the enhancement and confinement of the electric field. In particular, the realization of a microfluidic device to detect the dynamic oxidation state of EVOO, working in the UV-VIS spectral range, is presented.

Tran et al. [5] demonstrate the enhancement of fluorescence emitted by dye molecules coupled with two surface plasmons, namely localized surface plasmons (LSPs) induced by silver nanoparticles (AgNPs) and surface plasmons supported by thin silver film. A layer of SiO₂ with both rhodamine 110 molecules and AgNPs on top is illuminated: the AgNPs increase the excitation rates of the dye molecules in their immediate vicinity thanks to LSP-induced enhancement. In addition, the Ag film induces surface plasmon-coupled waveguide modes, resulting in a waveguide-modulated version of surface plasmon-coupled emission (SPCE) for different thicknesses of SiO₂ in an inverse Kretschmann configuration. The authors show that the variation of SiO₂ thickness can control the fluorescence of SPCE, which allows for optimizing the waveguide structure to enhance the fluorescent signals. This introduces the possibility of obtaining a highly sensitive fluorescent analysis of biomedical and chemical substances.

In the work of Burratti et al. [6] the authors study a new method by which to determine Pb(II) ions in water, by following the fluorescence emission of a silver nanocluster colloidal solution (AgNC). In fact, when Pb(II) ions are present in the water, this causes an increase in the photoemission of the AgNCs solution. This increase in photoemission depends logarithmically on the concentration of Pb(II) ions, in the range of 2.5 to 40 µM. By linearizing the calibration points the authors determine and use a linear function for the extrapolation of the Pb(II) concentrations. Accuracy is estimated from the relative standard deviation (RSD) to be 21% and 10%, respectively, based on the highest to the lowest Pb(II) amount. Inductively coupled optical-plasma emission spectroscopy (ICP-OES) confirms the described method. The accuracy of the method is also calculated for intentionally polluted mineral waters, showing the analogous trend as for model water: the lower the concentration, the higher the accuracy of the method.

Otomalo et al. [7] reported the preparation of Au/Ag core-shell bimetallic nanocuboids NPs. These show complex plasmonic phenomena, with dipolar longitudinal modes and higher order transverse modes. The authors use the imprint of these modes in the ultrafast optical transient response measured by pump probe transient absorption (TA) spectroscopy, to explore the NP vibrational landscape. Bimetallic NPs undergo complex movements, involving the displacement of facets, edges and corners: the amplitude and frequency of these modes depend on the thickness of the Ag shell, as the silver charge changes the proportions and the NP mass. The contributions of the vibrational modes to the experimental TA spectra vary with the probe laser wavelength at which the signal is monitored. The authors, exploiting combined simulations of the elastic and optical properties, elucidate the effect of the mechanisms involved in the acoustic-plasmon coupling.

In the sensor design, detection range and sensitivity are two of the most important features to be considered. Wang et al. [8], synthesized gold nanostars (Au NSs) with an absorption peak in the near infrared region (822 nm) and proposed an Au NSs-based plasmonic colorimetric sensor for catechol (CC) detection with a wide detection range from 3.33 nM to 107 µM and a limit of detection (LOD) at 1 nM. The sensor mechanism was based on the effect of CC on silver ions (Ag⁺) that were reduced to form silver (Ag) coating on the surface of Au NSs, causing a blue-shift in the LSPR of Au NSs. The effect was proportional to the amount of CC, since with the increase of catechol the Ag coating on the surface was gradually nucleated, and the LSPR blue-shift carried on. The final results produce a wide LSPR shift of the absorption band (up to 276 nm) enabling an ultra-wide range and the ultrasensitive detection of CC.

Candrea et al. [9] in their work, pursued two different goals: to form a self-assembled monolayer (SAM) on a gold nanosurface and to correlate its formation to the nanosurface curvature. They prepared luminescent functionalized gold nanoparticles of different shapes. In particular, they used thiolate bipyridine (Bpy-SH) functionalization and investigated the SAM formation on the basis of the photo-physics of Bpy-SH. They found that the fluorescence wavelength and the excited-state lifetime of Bpy-SH were strongly correlated to the formation of aggregates within SAMs, and at the same time they underlined how the nature of the aggregates is correlated to the shape of the nanoparticles. Micro-Raman spectroscopy investigation was used to test the surface enhanced Raman spectroscopy effect of gold nanoparticles on thiolate bipyridine forming SAMs.

An alternative and efficient method by which to tailor the optical properties for optoelectronic applications is represented by the combination of metallic nanostructures with 2D transition metal dichalcogenides. Ferrera et al. [10] synthesized monolayer flakes of WS₂ by chemical vapor deposition and transferred them onto a densely packed array of Au nanoparticles. The optical properties were measured as a function of the thickness of a dielectric spacer intercalated between the two materials and as a function of the temperature (75–350 K). They found that the coupling between the localized surface plasmon resonance of Au NPs and the WS₂ exciton was dependent on the temperature and spacer-thickness, and that the closely packed morphology of the plasmonic array promotes a high confinement of the electromagnetic field in regions inaccessible to the WS₂ deposited on top.

Gram-negative bacteria (in particular their outer membrane) contains bacterial endotoxins known as Lipopolysaccharides (LPS). These large molecules have a strong toxic effect that can cause severe detrimental effects on human beings such as fever, hypotension, shock, and even death. Endotoxins are often present in the environment and medical implants and represent undesirable contaminations of pharmaceutical preparations and medical devices. For these reasons innovative and easy methods for the detection of LPS will be of crucial importance. Colombelli et al. [11] reported on an interesting approach for the sensitive detection of LPS by exploiting optical features of nanoplasmonic transducers supporting LSPRs. Ordered arrays of gold nano-prisms and nano-disks have been realized via nanosphere lithography. The authors developed a miniaturized lab-on-a-chip (LOC) platform integrated with the transducers and functionalized with specific antibodies as sensing elements for the detection of LPS. The sensor mechanism is based on a spectral shift of the plasmonic resonance peak of the transducers when the investigated analyte interacts with the specific antibodies anchored on protein A on the sensor chips. A good linear relationship between peak shifts and the LPS concentration has been demonstrated with a LOD down to 5 ng/mL. Integration with specific microfluidic devices reveals the possibility of producing prototypal compact devices to be used on pharmaceutical products.

Another interesting context is represented by the bacteriophage (phage) therapy. In this field, the development of innovative methods permitting multiplexed, parallel phage susceptibility testing (PST) prior to the formulation of personalized phage cocktails, is very important for patients with antimicrobial-resistant bacterial infections. In this context, O'Connell et al. [12] proposed a method based on surface plasmon resonance imaging (SPRi) and phase imaging as rapid (<2 h) candidates for PST in the broth phase. Biosensing layers composed of arrays of different phages (44AHJD, P68, and gh-1) were covalently linked on the surface of an SPRi prism and exposed to liquid culture of either *Pseudomonas putida* or methicillin-resistant *Staphylococcus aureus*. The measurement of reflectivity as a function of time reveals the susceptibility of the challenge bacteria to the immobilized phage strains. Surface plasmon resonance imaging shows that on-target regions increase in reflectivity more slowly, stabilizing later and to a lower level compared to off-target regions. The measured response time was of the order of 30 min in both the SPRi and phase imaging methods demonstrating a strong potential for developing real devices.

In conclusion, as the guest editors of this Special Issue, we are aware that the wealth of innovations of new compounds and tools related to nanomaterials based on noble metals

that are rapidly developing in the field of multidisciplinary research, cannot be collected in a single volume. Nevertheless, we are satisfied with the topics collected in this Special Issue and the care and proficiency with which they have been addressed and we are sure that this collection will contribute to the developing field of research in this area, providing our readers with a broad and updated overview of this topic.

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