Optical Fiber Probe Based on Localized Surface Plasmon Resonance of Gold Nanostructures for Chemical Sensing

Amin Moslemi[1], Lucia Sansone[2], Flavio Esposito[1][a], Carlos Marques[3,4], Stefania Campopiano[1][b], Michele Giordano[2] and Agostino Iadicicco[1][c]
[1]*Department of Engineering, University of Naples "Parthenope", 80143 Naples, Italy*
[2]*Institute for Polymers, Composites, and Biomaterials, National Research Council of Italy, IPCB-CNR, 80055 Portici, Italy*
[3]*CICECO – Aveiro Institute of Materials, Physics Department, University of Aveiro, Aveiro 3810-193, Portugal*
[4]*Department of Physics, VSB – Technical University of Ostrava, Ostrava 70800, Czech Republic*

Keywords: Optical Fiber Sensors, Localized Surface Plasmon Resonance, Plasmonics, Biosensors, Chemical Sensors.

Abstract: In this study, we present an experimental investigation of highly sensitive optical fiber sensors utilizing localized surface plasmon resonance (LSPR), achieved by depositing gold nanoparticles (NP) onto uncladded silica multi-mode fiber. This setup takes advantage of the unique optical characteristics of optical fiber sensors and plasmonic resonance provided by gold NPs. The experimental results demonstrated a maximum sensitivity of about 130 nm/RIU in water solution, for an LSPR wavelength at 560 nm. As a study case, the sensor was used to detect Thiram, a common agricultural pesticide, exhibiting a wide detection range from 10 nM to 100 µM, with a significant wavelength shift up to 4 nm. Moreover, a preliminary study involving the use of nanostar-based optical fiber sensors is comparatively provided. The highest sensitivity makes this approach highly promising for a range of applications, including environmental monitoring, biomedical diagnostics, and chemical detection.

1 INTRODUCTION

Localized surface plasmon resonance (LSPR) refers to the coherent oscillation of surface conduction electrons in noble metal nanoparticles induced by electromagnetic radiation at the nanoscale (Ma et al., 2021; Mayer & Hafner, 2011). It is widely utilized for sensing applications, with the LSPR absorption band and its spectral position highly dependent on the electrical properties of the noble metal (typically gold or silver), the size and shape of the nanostructures, and the dielectric properties of the surrounding medium (Yaghubi et al., 2020). Consequently, these devices are emerging as advanced sensors for chemical and biological detection due to their exceptional sensitivity to variations in the surrounding medium refractive index (SRI) (Jeon et al., 2019; Ma et al., 2021).

While early investigations of LSPR focused on spherical gold nanoparticles (NPs), researchers are now exploring a variety of sizes, shapes, and materials. Nanostars (NSs) and nanorods (NRs), for example, have different LSPR attenuation bands compared to spherical NPs due to variations in their shape and structural properties. These variations allow for the generation of multiple resonances and the ability to tune both the resonance wavelength and sensitivity (He et al., 2020; Ringe et al., 2010; Shabaninezhad & Ramakrishna, 2019; Ueno et al., 2007). As a result, nanostructures with increased aspect ratio offer high sensitivity for label-free biosensing and chemical detection (Yuan et al., 2012). For instance, Nguyen et al. introduced a sensitive nanoplasmonic biosensor capable of detecting two key epigenetic biomarkers using NSs: methyl-CpG and MBD2, with detection limits of one 5-methylcytosine molecule and 125 fM MBD2, respectively (Nguyen et al., 2015). Dondapati et al. reported streptavidin binding to biotin-modified NSs causing a plasmon resonance shift of 2.3 nm at

[a] https://orcid.org/0000-0003-1187-5825
[b] https://orcid.org/0000-0002-2987-9122
[c] https://orcid.org/0000-0002-3540-7316

Moslemi, A., Sansone, L., Esposito, F., Marques, C., Campopiano, S., Giordano, M. and Iadicicco, A.
Optical Fiber Probe Based on Localized Surface Plasmon Resonance of Gold Nanostructures for Chemical Sensing.
DOI: 10.5220/0013395000003902

In *Proceedings of the 13th International Conference on Photonics, Optics and Laser Technology (PHOTOPTICS 2025)*, pages 157-162
ISBN: 978-989-758-736-8; ISSN: 2184-4364

concentrations as low as 0.1 nM. (Dondapati et al., 2010). Finally, Hashemi et al. developed a highly sensitive electrochemical nanosensor to detect monoclonal IgG antibodies against the SARS-CoV-2 S1 protein in blood within 1 minute. The sensor, utilizing activated graphene and gold NSs, achieved an ultra-low detection limit of $0.18 \cdot 10^{-19}$ %V/V (Alireza Hashemi et al., 2021).

Fiber optic sensors are increasingly popular due to their advantages, including high sensitivity, improved signal-to-noise ratio, cost-effectiveness, and the ability to operate in harsh environments. These characteristics make them suitable for a wide range of chemical and biological sensing applications (Choudhary et al., 2025; Gandhi et al., 2019; Ricciardi et al., 2015).

While there is extensive literature on using spherical NPs with optical fiber sensors, the integration of other types of nanostructures with optical fibers (Cennamo et al., 2013; Xiao et al., 2025), however, is less explored, with only a few studies available. For example, Cennamo et al. introduced a novel optical chemical sensor that uses molecularly imprinted polymer and NSs on plastic optical fibers for the selective detection of Trinitrotoluene in aqueous solutions. The device achieves a sensitivity of $8.3 \cdot 10^{5}$ nm/M, 30 times higher than previous gold layer SPR sensors (Cennamo et al., 2015). In another study, Dos Santos et al. utilized high aspect-ratio gold-silver nanorods, which demonstrated a refractive index sensitivity of 1720 nm/RIU at 1350 nm (O-band) and 2325 nm/RIU at 1550 nm (L-band). Using a side-polished optical fiber, glyphosate detection they achieved a detection limit improvement from 724 to 85 mg/L by shifting to the C/L bands (dos Santos et al., 2025).

In this work, fiber optic probe based on spherical gold nanoparticles properly grafted onto etched multi-mode fiber (MMF) surface are evaluated for chemical sensing applications. Specifically, its performance has been assessed through the detection of a dangerous compound like Thiram pesticide. Moreover, a preliminary comparative study on the use of gold-silver NSs in place of gold NPs is also presented.

2 FABRICATION OF GOLD NANOPARTICLES AND THEIR CHARACTERIZATION

Gold NPs with spherical shapes were synthesized using the well-assessed Turkevich method (Moslemi et al., 2024). Figure 1(A) presents the UV-Vis spectra recorded with an Agilent Cary 60 spectrophotometer using quartz cuvettes, showing the results for prepared NP samples. The absorbance peak centred at 531 nm is clearly visible. The morphological characterization is provided by TEM images as in Figure 1(B) where an average diameter of 40 nm can be observed.

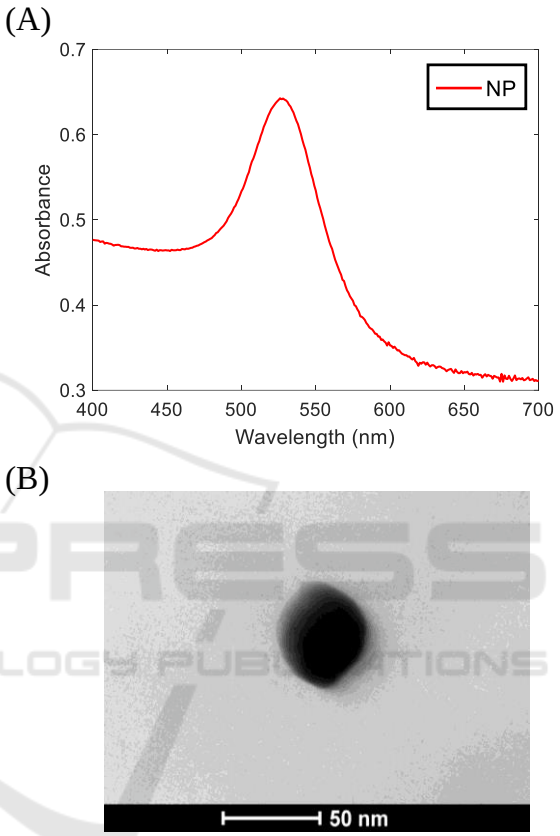

Figure 1: (A) UV-Vis spectra of gold NPs in solution; and (B) TEM image of gold NP.

3 FABRICATION AND CHARACTERIZATION OF THE OPTICAL FIBER PROBE

3.1 Fabrication of the Probe

The basic sensor configuration is illustrated in Figure 2. It features an etched silica MMF with a mirrored tip to enable reflected signal readout. The uncladded etched region of the fiber is coated with metallic nanostructures. The reflected signal from the probe exhibits an attenuation band corresponding to the excitation of LSPR.

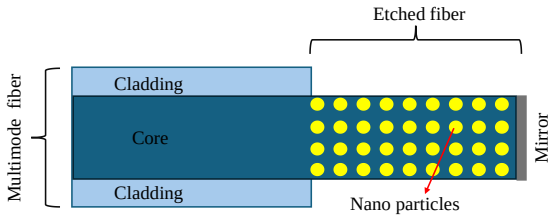

Figure 2: Schematic of the optical fiber probe.

For the fabrication, a few cm long piece of a 105/125 µm core/cladding MMF model Thorlabs FG105LCA was etched for 25 minutes using 24% hydrofluoric acid until the diameter was reduced to 95 µm, i.e. to remove the cladding and expose the core. This allows the core modes to interact with external media via the evanescent wave.

The silica surface of the etched fiber is then silanized to facilitate the grafting of metallic nanostructures. The process involves the following steps. First, the fiber is immersed in piranha solution for one hour to promote the formation of hydroxyl groups, followed by thorough rinsing with water. Next, it is immersed in an 5% w/w (3-Aminopropyl)triethoxysilane (APTES) solution for two hours to achieve surface silanization (Ben Haddada et al., 2013). Afterward, the fiber is cleaned with acetone and left to air-dry overnight.

Finally, to enable the reflection-based readout approach, the fiber tip was cut and coated with a silver layer to create a mirror.

Next, the functionalized fiber was immersed in the metallic nanostructure solution prepared as detailed in Section 2 for approximately four hours. The fiber was then removed from the solution, left to dry overnight, and washed five times with water to remove loosely attached nanostructures.

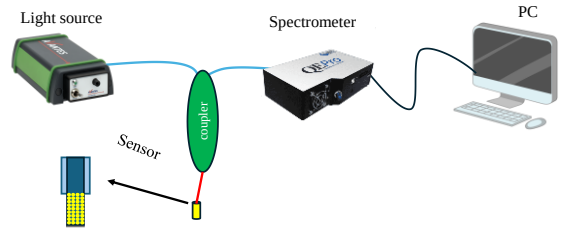

Figure 3: Schematic of the optoelectronic readout setup.

An optoelectronic readout setup is necessary to monitor the reflection spectrum of the so-prepared sensing probe. The schematic of the setup is shown in Figure 3: it consists of a broadband light source (Avantes AvaLight-HAL-S-Mini) to provide incident light. The light source is connected to a 50:50 MMF coupler, while the transducer is connected to the output of the coupler. The coupler then directs the reflected signal to the spectrometer (Ocean Optics HR2000+), and the data is displayed on a PC for storage and analysis.

Figure 4 presents the reflected spectra of the samples coated with the NPs, when immersed in water environment. The spectra feature an attenuation band indicative of LSPR. Specifically, the NP-based sensor exhibits an attenuation band centred at 560 nm, in agreement with nanostructure spectra taken in solution in Figure 1. The slight difference is attributed to the fact that now the gold NPs are deposited onto optical fiber surface.

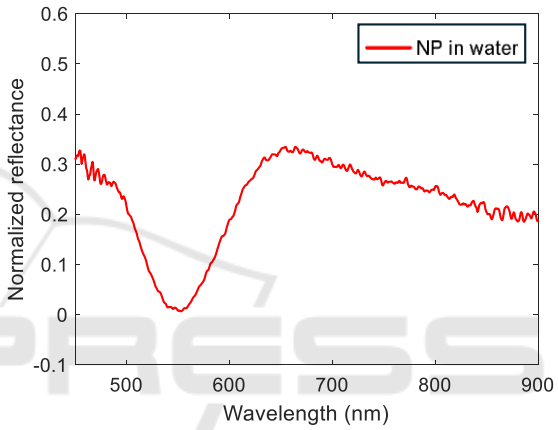

Figure 4: Reflection spectra of the transducer with NP deposition when the surrounding medium is water.

3.2 Sensitivity to Bulk Surrounding Refractive Index

For this study, the sensitivity to surrounding refractive index (SRI) medium changes of the NP sample was evaluated to compare their sensing performance based on synthesis and morphology. Solutions with varying refractive indices, ranging from SRI = 1.33-1.40, were prepared by mixing deionized water and glycerine.

Subsequently, the sensor was sequentially immersed in the prepared solutions to monitor their response. The corresponding wavelength shifts of the attenuation band are depicted in Figure 5, where experimental data points are shown as markers, and linear fits are represented by solid lines. The calculated SRI sensitivity is about 130 nm/RIU (Zhang et al., 2023).

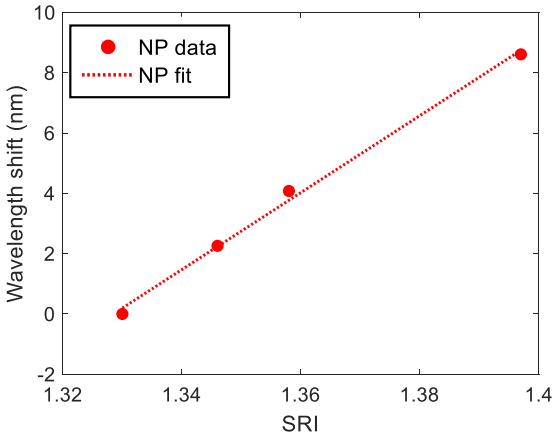

Figure 5: Wavelength shift as a function of the SRI for NP-based sensor.

4 STUDY CASE: DETECTION OF PESTICIDE

In this section, NP-based sensor was analyzed for its capability to detect Thiram pesticide, a compound known to interact strongly with gold nanostructures through its thiol groups. This binding event directly affects the LSPR of the nanostructures, manifesting as a wavelength shift in the attenuation band of the sensor (Zhang et al., 2023).

Thiram solutions with concentrations ranging from 10 nM to 100 µM were prepared in water to perform this analysis. The sensor was initially stabilized for the test by immersing them in deionized water for 30 minutes. Following stabilization, it was exposed sequentially to Thiram solutions of increasing concentrations. Each immersion lasted approximately 30 minutes, during which reflected spectra were recorded every 30 seconds. Experiments were performed under controlled temperature within ±0.5 °C.

Spectral results are reported in Figure 6(A), where a progressive redshift in the LSPR attenuation band was observed as the Thiram concentration increased from 10 nM to 100 µM, confirming the binding interaction between Thiram and the gold nanostructures. Specifically, a maximum wavelength shift of about 4 nm was achieved in the investigated range of Thiram concentrations, allowing seamless detection down to 10 nM.

5 PRELIMINARY RESULTS BASED ON GOLD-SILVER NANOSTARS

Recently, exotic noble metallic structures have been widely investigated to enhance the plasmonic interaction with target medium in order to reduce the minimum detectable concentrations. On this line of argument, in this section preliminary analysis on the possibility to synthesize and investigate gold-based NSs instead of gold NPs is reported.

NSs were synthesized using a seed-mediated growth method. To prepare the seed solution, 15 mL of 1% citrate solution was added to 100 mL of a boiling 1 mM tetrachloroauric acid $HAuCl_4$ solution while stirring vigorously. After 15 minutes of boiling, maintaining the volume, the mixture was cooled and filtered through a 0.22 µm nitrocellulose membrane, then stored at 4 °C for long-term use. For NS synthesis, 100 µL of the citrate-stabilized seed solution was added to 10 mL of 0.25 mM $HAuCl_4$ solution, along with 10 µL of 1 M HCl, in a 20 mL glass vial at room temperature under moderate stirring (700 rpm). Then, 100 µL of silver nitrate (1.5 mM) and 50 µL of ascorbic acid (100 mM) were added simultaneously. The solution was stirred for 30 seconds, during which its colour changed rapidly from light red to blue or greenish black. The nucleation process was halted by centrifuging the solution at 3000-5000 rcf for 15 minutes in a 15 mL tube. The solution was then redispersed in deionized water, filtered through a 0.22 µm nitrocellulose membrane, and stored at 4 °C for long-term preservation.

Once the NS solution is prepared, a new optical fiber sample has been prepared by the same procedure reported in Section 3.1. In NS-based sensors, the resonance wavelength is strongly dependent on the NS fabrication parameters. A deep study involving numerical and experimental results is currently in progress.

Figure 6(B) shows the performance of NS-based device for the detection of Thiram. The experiment was repeated in the same way as for NP-based sensor. The sensor exhibited a significant increase of the sensitivity with a maximum wavelength shift of 8 nm in the range of concentrations 10 nM - 10 µM. These concentrations are significantly lower than those explored by UV-Vis-based methods and comparable to those investigated by SERS (Moslemi et al., 2024), holding promise for future application in bio-chemical sensing domain.

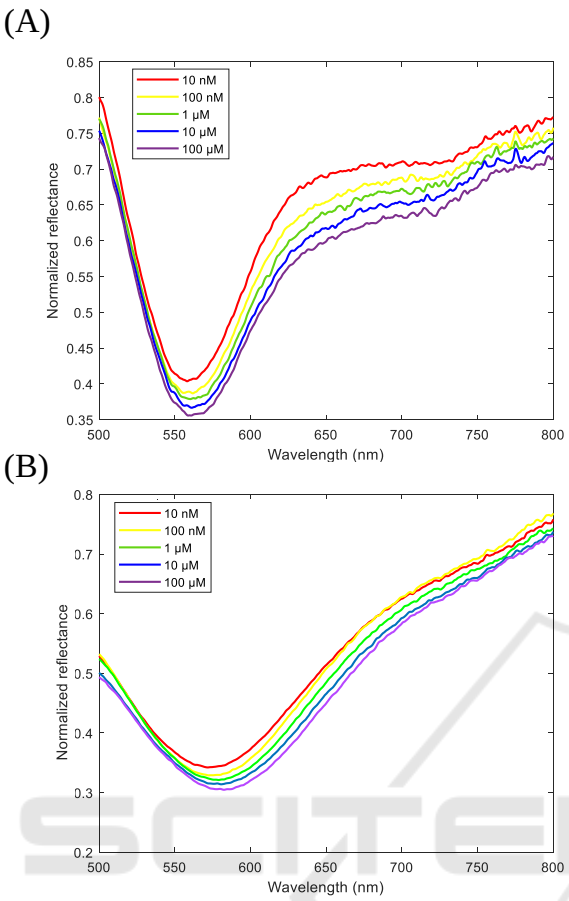

Figure 6: Spectra of LSPR fiber optic probes during the detection of pesticide Thiram at different concentrations, employing (A) NPs and (B) NSs.

6 CONCLUSIONS

In summary, this study introduces a highly sensitive LSPR-based fiber optic sensors employing gold nanostructures deposited on uncladded silica multimode fiber. Results first revealed an SRI sensitivity of approximately 130 nm/RIU (in a water environment) for an LSPR wavelength near 560 nm leveraging gold NPs.

The sensor performance was further evaluated for detecting Thiram pesticide in water, achieving a wide detection range (10 nM to 100 µM) with a maximum wavelength shift of 4 nm for NP-based device.

Moreover, preliminary results on another device employing NSs highlighted enhanced promising performance. These straightforward and cost-effective designs allow detection of very low analyte concentrations compared to conventional SERS and UV-Vis-based methods, making them an attractive solution for applications in digital agriculture, environmental monitoring, and diverse chemical detection scenarios.

ACKNOWLEDGEMENTS

This work was performed within the project "Monitoring of Honeybee Immunomodulation and Resilience to Stress Factors by Fiber Optic Technology" (MoBeeFO) CUP I53D23000390006 under PRIN 2022 grant financed by the European Union – Next Generation EU, Mission 4 Component 1 and Italian Ministry of University and Research. This work was also developed within the scope of the projects CICECO (LA/P/0006/2020, UIDB/50011/2020 & UIDP/50011/2020) and DigiAqua (PTDC/EEI-EEE/0415/2021), financed by national funds through the (Portuguese Science and Technology Foundation/MCTES (FCT I.P.)). The research was co-funded by the financial support of the European Union under the REFRESH – Research Excellence For REgion Sustainability and High-tech Industries project number CZ.10.03.01/00/22_003/0000048 via the Operational Programme Just Transition.

REFERENCES

Alireza Hashemi, S., Bahrani, S., Mojtaba Mousavi, S., Omidifar, N., Ghaleh Golab Behbahan, N., Arjmand, M., Ramakrishna, S., Bagheri Lankarani, K., Moghadami, M., Shokripour, M., Firoozsani, M., & Chiang, W.-H. (2021). Ultra-precise label-free nanosensor based on integrated graphene with Au nanostars toward direct detection of IgG antibodies of SARS-CoV-2 in blood. *Journal of Electroanalytical Chemistry*, *894*, 115341. https://doi.org/10.1016/j.jelechem.2021.115341

Ben Haddada, M., Blanchard, J., Casale, S., Krafft, J.-M., Vallée, A., Méthivier, C., & Boujday, S. (2013). Optimizing the immobilization of gold nanoparticles on functionalized silicon surfaces: amine- vs thiol-terminated silane. *Gold Bulletin*, *46*(4), 335–341. https://doi.org/10.1007/s13404-013-0120-y

Cennamo, N., D'Agostino, G., Donà, A., Dacarro, G., Pallavicini, P., Pesavento, M., & Zeni, L. (2013). Localized Surface Plasmon Resonance with Five-Branched Gold Nanostars in a Plastic Optical Fiber for Bio-Chemical Sensor

Implementation. *Sensors*, *13*(11), 14676–14686. https://doi.org/10.3390/s131114676

Cennamo, N., Donà, A., Pallavicini, P., D'Agostino, G., Dacarro, G., Zeni, L., & Pesavento, M. (2015). Sensitive detection of 2,4,6-trinitrotoluene by tridimensional monitoring of molecularly imprinted polymer with optical fiber and five-branched gold nanostars. *Sensors and Actuators B: Chemical*, *208*, 291–298. https://doi.org/10.1016/j.snb.2014.10.079

Choudhary, S., Esposito, F., Sansone, L., Giordano, M., Campopiano, S., & Iadicicco, A. (2025). Polyphenylene oxide based lossy mode resonance fiber sensor for the detection of volatile organic and inorganic compounds. *Optics & Laser Technology*, *180*, 111519. https://doi.org/10.1016/j.optlastec.2024.111519

Dondapati, S. K., Sau, T. K., Hrelescu, C., Klar, T. A., Stefani, F. D., & Feldmann, J. (2010). Label-free Biosensing Based on Single Gold Nanostars as Plasmonic Transducers. *ACS Nano*, *4*(11), 6318–6322. https://doi.org/10.1021/nn100760f

dos Santos, P. S. S., Mendes, J. P., Pastoriza-Santos, I., Juste, J.-P., de Almeida, J. M. M. M., & Coelho, L. C. C. (2025). Gold-coated silver nanorods on side-polished singlemode optical fibers for remote sensing at optical telecommunication wavelengths. *Sensors and Actuators B: Chemical*, *425*, 136936. https://doi.org/10.1016/j.snb.2024.136936

Gandhi, M. S. A., Chu, S., Senthilnathan, K., Babu, P. R., Nakkeeran, K., & Li, Q. (2019). Recent Advances in Plasmonic Sensor-Based Fiber Optic Probes for Biological Applications. *Applied Sciences*, *9*(5), 949. https://doi.org/10.3390/app9050949

He, M.-Q., Yu, Y.-L., & Wang, J.-H. (2020). Biomolecule-tailored assembly and morphology of gold nanoparticles for LSPR applications. *Nano Today*, *35*, 101005. https://doi.org/10.1016/j.nantod.2020.101005

Jeon, H. Bin, Tsalu, P. V., & Ha, J. W. (2019). Shape Effect on the Refractive Index Sensitivity at Localized Surface Plasmon Resonance Inflection Points of Single Gold Nanocubes with Vertices. *Scientific Reports*, *9*(1), 13635. https://doi.org/10.1038/s41598-019-50032-3

Ma, S., Yang, D.-J., Ding, S.-J., Liu, J., Wang, W., Wu, Z.-Y., Liu, X.-D., Zhou, L., & Wang, Q.-Q. (2021). Tunable Size Dependence of Quantum Plasmon of Charged Gold Nanoparticles. *Physical Review Letters*, *126*(17), 173902. https://doi.org/10.1103/PhysRevLett.126.173902

Mayer, K. M., & Hafner, J. H. (2011). Localized Surface Plasmon Resonance Sensors. *Chemical Reviews*, *111*(6), 3828–3857. https://doi.org/10.1021/cr100313v

Moslemi, A., Sansone, L., Esposito, F., Campopiano, S., Giordano, M., & Iadicicco, A. (2024). Optical fiber probe based on LSPR for the detection of pesticide Thiram. *Optics & Laser Technology*, *175*, 110882. https://doi.org/10.1016/j.optlastec.2024.110882

Nguyen, A. H., Ma, X., & Sim, S. J. (2015). Gold nanostar based biosensor detects epigenetic alterations on promoter of real cells. *Biosensors and Bioelectronics*, *66*, 497–503. https://doi.org/10.1016/j.bios.2014.12.015

Ricciardi, A., Crescitelli, A., Vaiano, P., Quero, G., Consales, M., Pisco, M., Esposito, E., & Cusano, A. (2015). Lab-on-fiber technology: a new vision for chemical and biological sensing. *The Analyst*, *140*(24), 8068–8079. https://doi.org/10.1039/C5AN01241D

Ringe, E., McMahon, J. M., Sohn, K., Cobley, C., Xia, Y., Huang, J., Schatz, G. C., Marks, L. D., & Van Duyne, R. P. (2010). Unraveling the Effects of Size, Composition, and Substrate on the Localized Surface Plasmon Resonance Frequencies of Gold and Silver Nanocubes: A Systematic Single-Particle Approach. *The Journal of Physical Chemistry C*, *114*(29), 12511–12516. https://doi.org/10.1021/jp104366r

Shabaninezhad, M., & Ramakrishna, G. (2019). Theoretical investigation of size, shape, and aspect ratio effect on the LSPR sensitivity of hollow-gold nanoshells. *The Journal of Chemical Physics*, *150*(14). https://doi.org/10.1063/1.5090885

Ueno, K., Juodkazis, S., Mino, M., Mizeikis, V., & Misawa, H. (2007). Spectral Sensitivity of Uniform Arrays of Gold Nanorods to Dielectric Environment. *The Journal of Physical Chemistry C*, *111*(11), 4180–4184. https://doi.org/10.1021/jp068243m

Xiao, A., Wu, X., Zheng, J., Huang, Y., Xu, A., & Guan, B.-O. (2025). Sensitivity evaluation of an optical microfiber featuring interfaces with various gold nanoparticle morphologies: Application to the GFAP detection. *Biosensors and Bioelectronics*, *268*, 116901. https://doi.org/10.1016/j.bios.2024.116901

Yaghubi, F., Zeinoddini, M., Saeedinia, A. R., Azizi, A., & Samimi Nemati, A. (2020). Design of Localized Surface Plasmon Resonance (LSPR) Biosensor for Immunodiagnostic of E. coli O157:H7 Using Gold Nanoparticles Conjugated to the Chicken Antibody. *Plasmonics*, *15*(5), 1481–1487. https://doi.org/10.1007/s11468-020-01162-2

Yuan, H., Khoury, C. G., Hwang, H., Wilson, C. M., Grant, G. A., & Vo-Dinh, T. (2012). Gold nanostars: surfactant-free synthesis, 3D modelling, and two-photon photoluminescence imaging. *Nanotechnology*, *23*(7), 075102. https://doi.org/10.1088/0957-4484/23/7/075102

Zhang, Y., Ding, L., Zhao, J., Jiang, X., & Ma, F. (2023). Localized Surface Plasmon Resonance- Based Fiber Optic Biosensor for Acetylcholine Detection. *IEEE Sensors Journal*, *23*(21), 25987–25995. https://doi.org/10.1109/JSEN.2023.3304619