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VOC Detection: Hope or Hype? A Preliminary Study to Overcome Many Challenges

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***Abstract* — Volatile organic compounds (VOCs) are usually small-size by products of cellular metabolic activity, spreading through bodily fluids (such as breath), that can be regarded as pathophysiological biomarkers. A promising method for developing VOC sensors involves gold nanoparticles (AuNP) to create a lock-and-key system. The concentration of the target molecules interacting with the AuNP detectors can determine a change of electrical resistance and allow VOC concentration to be traced. In this paper, we present our preliminary results on ethanol detection, considered as a model molecule for VOCs, through AuNP synthesis and deposition on cotton, as a flexible and biodegradable substrate. An aqueous gold solution was prepared by using chloroauric acid as gold precursor and polyvinylpyrrolidone as reducing/dispersing agent. The cotton substrate was dip-coated in the solution. The optical characterization in the UV-vis range of both solution and coated cotton revealed the presence of around 20 nm diameter particles associated to a peak at 550 nm. The sample electrical characterization showed different behavior before and after spraying a 40% ethanol solution. In particular, the presence of ethanol brought to an average resistance variation of about 5 orders of magnitude in the 1Hz-1MHz range. Resistance change is probably due to the specific adsorption of the ethanol molecules and the gold nanoparticles/cotton interface. This behavior can be also observed at very low EtOH concentration (up to 1%v/v), showing a promising sensor sensibility. Because of the high capability of AuNP to interact with a wide range of biologically relevant molecules and specifically with the C-OOH or C-OH groups of the VOCs, these pilot results are promising for future applications concerning VOC detection.**

Keywords – Volatile Organic Compound (VOC), gold nanoparticles (AuNPs), ethanol detection, textile, gas sensing

I. Introduction

Human health has always been a challenge for governments focused on a patient-centric point of view. The investigation on new technologies (wearable devices, telemedicine tools, innovative sensing mechanism) could enable smart treatment paths, especially useful for non-autonomous people [1-5]. The recent COVID-19 pandemic has stressed healthcare shortcomings. In fact, patients' demand has not been matched by the small number of technicians, long waiting times, and sometimes outdated equipment. Many studies suggest that breath analysis can be a promising diagnostic alternative since it is a non-invasive, easy-to-collect and user-friendly technique [6-8]. Since exhaled breath is a mixture of volatile organic compounds (VOCs) coming from cellular metabolic activity, it can be indicative of the health status [9-11]. Ethanol (EtOH) is one of the most common exhaled VOCs. Being a byproduct of the microbial fermentation of carbohydrates in the gastrointestinal tract [12, 13], EtOH can be considered a probe for diseases like diabetes mellitus [14], cystic fibrosis [15], fatty liver disease and alcohol intoxication [16, 17]. Buszewski et al. investigated analytic techniques for VOC molecular probe detection with diagnostic purposes [18], underlining the high accuracy and sensitivity of these methods. Furthermore, innovation in nanomaterial-, optical- and semiconductor-based sensors are useful in lowering costs, improving response time and reducing the need of skilled professionals. Many researchers highlight gold nanoparticles as a key point in the development of fast and sensitive bio detectors [19-21]. Besides, new kinds of substrates, such as paper and textiles, have been proposed for sustainable, low-cost, simple sensing methods [22]. Therefore, such porous materials show a much higher surface-to-volume ratio with respect to standard substrates, which result into maximized sensor-VOC exposure, enhancing sensitivity and limits of detection [23-26]. Textile substrates can represent an enabling key for integrated sensing in wearable devices, such as face masks [18]. Indeed, among the clinical, social, economic and political consequences of the recent COVID-19 pandemic, face masks have become a daily routine for a large part of the world's population [27, 28], gaining also a growing scientific attention as smart, portable, user-friendly platform with embedded sensors [29-31].

In this study we present a chemo-sensor, based on gold nanoparticles as sensitive layer, for ethanol detection, using a cotton textile as sensor's substrate. The operation principle of our device is based on the interaction between EtOH and AuNPs, which takes place through hydroxyl bonds influencing the impedance sensor response. Preliminary results show a large variation of sensor's resistance after spraying ethanol on the substrate, suggesting that the sensor can be used for the detection of different VOCs, due to the aptitude of AuNP to link to the functional groups of the volatile organic compounds, and encouraging us to optimize the presented device for future applications.

II. EXPERIMENTAL DETAILS

A. Substrate Preparation

The fabrication process is comprised of three successive steps: synthesis, deposition and drying, as depicted in Figure 1. Distilled water and Tetra-Chloroauric (III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.995%) were used for the gold precursor preparation. Polyvinylpyrrolidone (PVP10, average mol wt 10,000) was used as reducing/surfactant agent in the nanoparticle agglomeration. The substrate chosen for the coating was a cotton textile (Cod.558–79). All the reagents were purchased from Sigma Aldrich, while the cotton sheets were bought from RS Components. The synthesis was carried out at ambient conditions (Temperature = 23°C, Relative Humidity = 60%) by adding PVP and the gold precursor into a beaker containing 50 ml of H2O (inlet in the left) under stirring - through a RCT basic, IKA Magnetic Stirrer. The central picture shows the dip coating of a cotton substrate in the previously-synthesized, violet solution. Subsequently, the wet sensor was left air drying for 3 h under the same operating setting (picture on the right).

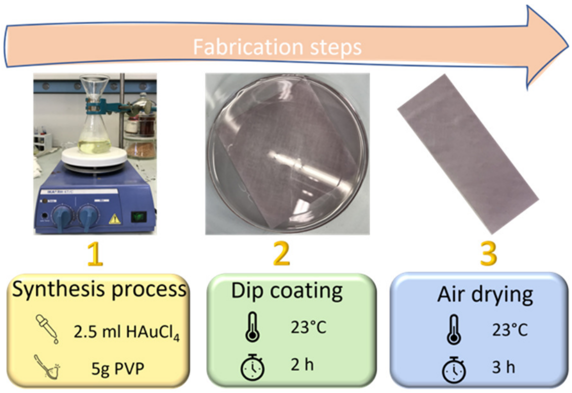

Figure 1. Sequential steps (1,2,3) involved in the fabrication process of a gold nanoparticles-coated cotton substrate: synthesis, coating and drying.

B. Substrate Characterization

Pristine and functionalized cotton fabric were characterized using a Scanning Electron Microscope (SEM) MIRA3 (from TESCAN, Brno, Czech Republic), a double beam spectrophotometer V-660 (Jasco, Tokio, Japan) and a Reference 3000 potentiostat (from Gamry Instruments, Philadelphia, Pennsylvania, USA). SEM investigation was carried out to reveal the morphological features of our sample before and after the AuNP deposition, UV-vis range absorption spectroscopy was employed to analyze optical properties, while the potentiostat measured the electrical properties of the device in a wide range of frequencies (1 Hz-1 MHz).

III. RESULTS AND DISCUSSION

Figures 2a and 2b reports the SEM analysis results on our samples. Figure 2a shows the image of pristine cotton and highlights the typical fibrous morphology of this kind of textile. Figure 2b shows the same fibers coated with nanoparticles (called AuNP-coated cotton). The AuNPs are the bright points in the image. Their presence is confirmed by the UV-vis absorption as reported in Figure 2c.

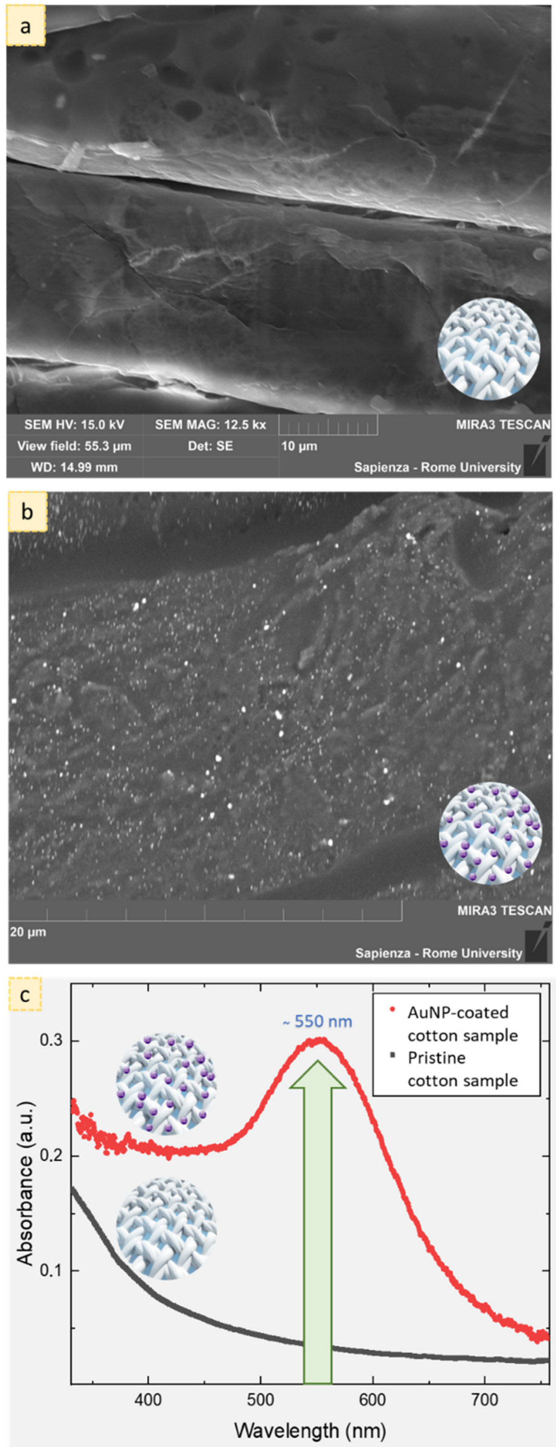

Figure 2. SEM analysis (a,b) and absorbance vs wavelength curves in the UV-vis range (c) for pristine and AuNP-coated cotton fibers.

Pristine cotton (black curve) showed no absorption in the investigated wavelength range, whereas a peak at around 550 nm was detected for AuNP-coated cotton (red curve). As demonstrated in [32], the absorbance-wavelength correlation is due to the presence of the nanoparticles. More specifically, such a peak reveals 15 nm-sized gold particle aggregates on the cotton surface.

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Finally, a VOC detection experiment was performed by means of electrochemical impedance spectroscopy (EIS) measurements: the impedance of both pristine and AuNP-coated cotton was measured in the frequency range 1 Hz-1 MHz, before and after spraying with a 40% ethanol solution. A sandwich configuration was utilized by inserting the cotton sensor between an aluminum top electrode and a copper bottom electrode. The metal electrodes were then connected to the impedance spectrometer. Figure 3a depicts the schematic measurement set up. Figure 3b reports the results in form of imaginary part, (Im(Z)), vs real part, Re(Z), impedance plot. Pristine cotton (black curve) was taken as reference. The red curve is the AuNP-coated cotton, while the blue curve (zoomed in Figure 3c) refers to the AuNP-coated cotton exposed to the VOC solution. AuNPs presence determines higher Im(Z) (probably ascribed to larger interfacial polarization) and lower Re(Z) values in the whole investigated frequency range.

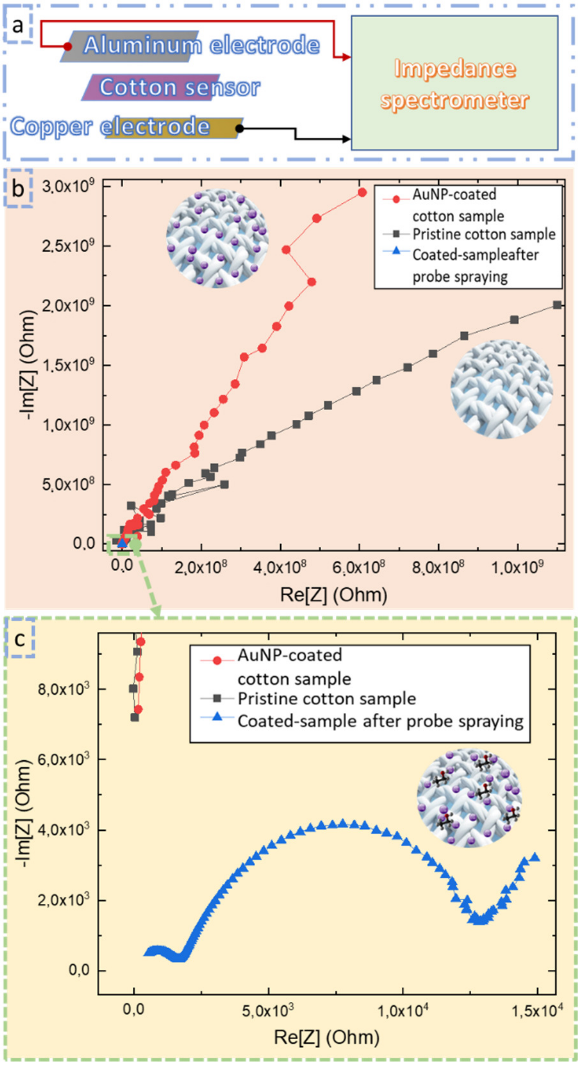

Figure 3. Operational setup for the EIS measurements (a) and plots underling the electrical behavioral changes (in the range 1 Hz – 1 MHz) of pristine cotton and AuNPs-coated samples before/after spraying the target solution (b, c).

After spraying the solution, both impedance imaginary and real parts decreased significantly. Particularly, the exposure to the EtOH solution reduced AuNP-coated cotton electrical resistance up to four orders of magnitude (from hundreds of MΩ to tens of kΩ). As reported in [33], the curves' shape (Figure 3 b, c) is directly related to specific molecule adsorption active sites at the gold nanoparticles/cotton interface. In particular, we ascribe the impedance change to the interaction between EtOH and AuNPs, which takes place through charge injection and transport mediated by the alcohol OH group. In fact, hydrogen -bonds (H-bonds) are formed between the R-OH moieties and PVP functional groups (N-containing rings and carbonyl groups. In order to corroborate such an assumption, we also investigated the effect of ethanol concentration on the electrical properties of the system and the results are reported in figure 4.

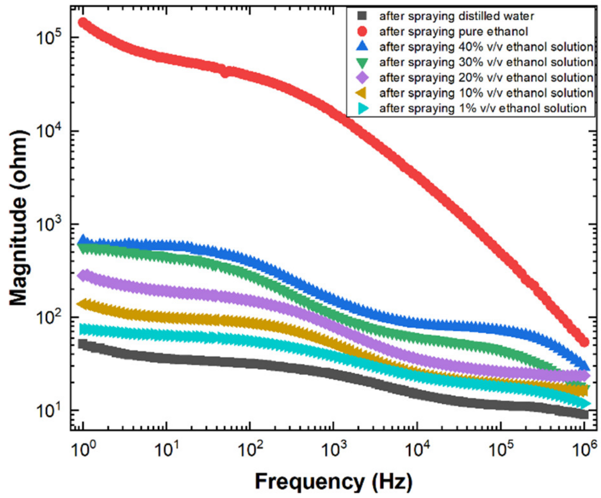

Figure 4. Impedance magnitude of AuNPs-coated samples sprayed with different concentrations of ethanol. Comparison with distilled water is also reported.

Interestingly, the higher the ethanol concentration the higher the impedance magnitude. Indeed, water allows for higher electron transfer and proton mobility by hydrogen bond via electronegative atoms on the PVP/gold surface. Thus, a Grotthus-like "jumping" mechanism may account for proton migration across the PVP-capped gold nanoparticles. Faster proton migration (i.e., lower impedance) occurs as the amount of ethanol in the solution is decreased (up to 1% v/v). Nonetheless, H-bonds stemming from ethanol-PVP interaction are still sufficient to bring about a significant impedance reduction with respect to the pristine (non-sprayed) samples, assuring a promising high sensitivity of the Au-functionalized cotton system.

IV. Conclusions

AuNP-coated textile suitable for chemiresistive detection of ethanol was investigated in this study. Optical characterization and SEM inspection verified the successful nanoparticles synthesis and deposition on a cotton sample. A preliminary test, consisting in the sample exposure to a EtOH solution (40% EtOH in water) and involving impedance measurements before and after the exposure, highlighted how AuNPs-EtOH interaction can decrease the resistance (i.e. the real component of the impedance) of multiple orders of magnitude. Furthermore, as the amount of ethanol into the sprayed solution was reduced, impedance (magnitude) decreased as well. This evidence suggests that protons in the analyte are prone to interact with AuNPs/PVP by hydrogen bonding, even at low analyte concentrations (up to 1% v/v of EtOH). These first promising results call for new tests in order to take advantage of AuNPs high capability to interact with a wide range of biologically relevant molecules. In particular, detection of various VOCs is envisaged due to the interaction of their functional groups with the AuNPs surface. In addition, the high scalability of green, simple and fast AuNP synthesis deposition process allow industrial implementation to undertaken. However, further, and deeply investigations are necessary to verify the effectiveness in detection of different VOCs, and to determine the limit of detection and selectivity.

References

[1] L. Chen, G. Zhang, L. Liu, and Z. Li, "Emerging biosensing technologies for improved diagnostics of COVID-19 and future pandemics.", *Talanta*, 225, p 121986, 2021, doi: 10.1016/j.talanta.2020.121986

[2] A. Haleem, M. Javaid, R. P.Singh, and R. Suman, "Telemedicine for healthcare: Capabilities, features, barriers, and applications", *Sensors international*, 2, 100117, 2021, doi: 10.1016/j.sintl.2021.100117

[3] M. Wu, and J. Luo, "Wearable technology applications in healthcare: a literature review.", *Online J. Nurs. Inform*, 23(3), 2019 (last access: 29/01/2024)

[4] Lewy, H. "Wearable technologies–future challenges for implementation in healthcare services.", *Healthcare technology letters*, vol. 2(1), pp. 2-5, 2015, doi: 10.1049/htl.2014.0104

[5] A. A. Seyhan and C. Carini, "Are innovation and new technologies in precision medicine paving a new era in patients centric care?", *Journal of translational medicine*, vol. 17, pp. 1-28, 2019

[6] T. Chen, T. Liu, T. Li, H. Zhao, and Q. Chen, 2021 "Exhaled breath analysis in disease detection", *Clinica Chimica Acta*, 515, pp 61-72, doi: 10.1016/j.cca.2020.12.036

[7] A. Manolis,"The diagnostic potential of breath analysis.", *Clin. Chem*, vol. 29(1), pp. 5-15, 1983, doi: 10.1093/clinchem/29.1.5

[8] T. H. Risby, and S. F. Solga, "Current status of clinical breath analysis", *Applied Physics B*, vol. 85, pp. 421-426, 2006, doi: doi.org/10.1007/s00340-006-2280-4

[9] W. Miekisch, J. K. Schubert, and G. F. Noeldge-Schomburg, "Diagnostic potential of breath analysis—focus on volatile organic compounds", *Clinica chimica acta*, 347(1-2), pp 25-39, 2004, doi: 10.1016/j.cccn.2004.04.023

[10] A. D.Wilson, "Advances in electronic-nose technologies for the detection of volatile biomarker metabolites in the human breath.", *Metabolites*, vol. 5(1), pp. 140-163, 2015, doi: 10.3390/metabo5010140

[11] J. Pereira, , P. Porto-Figueira, , C. Cavaco, , K.Taunk, , S. Rapole, , R. Dhakne, Nagarajaram H, and J. S. Câmara, "Breath analysis as a potential and non-invasive frontier in disease diagnosis: an overview.", *Metabolites*, vol. 5(1), pp. 3-55, 2015, doi: 10.3390/metabo5010003

[12] A. G. Antoshechkin, "On intracellular formation of ethanol and its possible role in energy metabolism" *Alcohol and Alcoholism*, 36(6), pp 608-608, 2001, doi: 10.1093/alcalc/36.6.608

[13] S. Nair, K. Cope, R. H. Terence, and Diehl, A. M., "Obesity and female gender increase breath ethanol concentration: potential implications for the pathogenesis of nonalcoholic steatohepatitis.", *The American journal of gastroenterology*, vol. 96(4), pp. 1200-1204, 2001, doi: 10.1016/S0002-9270(01)02265-1

[14] S. Das, S. Pal, and M. Mitra, "Significance of exhaled breath test in clinical diagnosis: a special focus on the detection of diabetes mellitus.", *Journal of medical and biological engineering*, vol. 36, pp. 605-624, 2016, doi: 10.1007/s40846-016-0164-6

[15] L. D. Bos, , S. Meinardi, , D. Blake, , and K. Whiteson,. "Bacteria in the airways of patients with cystic fibrosis are genetically capable of producing VOCs in breath.", *Journal of breath research*, vol. 10(4), p 047103, 2016, doi: 10.1088/1752-7163/10/4/04710

[16] S. Mojumder, T. Das, S. Das, N. Chakraborty, D.Saha, and M. Pal, "Y and Al co-doped ZnO-nanopowder based ultrasensitive trace ethanol sensor: A potential breath analyzer for fatty liver disease and drunken driving detection.", *Sensors and Actuators B: Chemical,* 372 p 132611, 2022, doi: 10.1016/j.snb.2022.132611

[17] S. F. Solga, A. Alkhuraishe, K. Cope, A. Tabesh, J. M. Clark, Torbenson, M., ... and Risby, T. H. "Breath biomarkers and non-alcoholic fatty liver disease: preliminary observations.", *Biomarkers,* vol. 11(2), pp 174-183, 2006, doi: 10.1080/13547500500421070

[18] B. Buszewski, D. Grzywinski, T. Ligor, , T. Stacewicz, Z. Bielecki, and J. Wojtas, "Detection of volatile organic compounds as biomarkers in breath analysis by different analytical techniques", *Bioanalysis*, vol. 5(18), pp 2287-2306, 2013, doi: 10.4155/bio.13.183

[19] M. K. Nakhleh, Y. Y. Broza, and H. Haick, "Monolayer-capped gold nanoparticles for disease detection from breath." *Nanomedicine,* vol. 9(13), pp. 1991-2002, 2014, doi: 10.2217/nnm.14.121

[20] N. U. Nazir, S. R. Abbas, H. Nasir, and I. Hussain, "Electrochemical sensing of limonene using thiol capped gold nanoparticles and its detection in the real breath sample of a cirrhotic patient.", *Journal of Electroanalytical Chemistry*, 905, p 115977, 2022, doi: 10.1016/j.jelechem.2021.115977

[21] F. J. Ibanez, and F. P. Zamborini, "Chemiresistive sensing of volatile organic compounds with films of surfactant-stabilized gold and gold– silver alloy nanoparticles.", *Acs Nano,* vol. 2(8), pp 1543-1552, 2008, doi: 10.1021/nn800109q

[22] G. N. Islam, A. Ali, and S.Collie, "Textile sensors for wearable applications: A comprehensive review.", *Cellulose,* vol. 27, pp. 6103-6131, 2020, doi: 10.1007/s10570-020-03215-5

[23] S. Casalinuovo, A. Buzzin, D. Caschera, S. Quaranta, F. Federici, L. Zortea, A.Brotzu, S.Natali, D. Puglisi, G. de Cesare, D. Caputo, "AuNP-coated cotton as VOC sensor for disease detection from breath." Proceedings of SIE 2022, *Springer Nature*, 2022, doi: 10.1007/978-3-031-26066-7_17

[24] S. Casalinuovo, D. Caschera, S. Quaranta, and D. Caputo, "AuNP-decorated textile as chemo resistive sensor for acetone detection", *IEEE Sensors Journal*, 2024 doi: 10.1109/JSEN.2023.3348693

[25] S. Casalinuovo, D. Caschera, , S. Quaranta, V. Genova, , A. Buzzin, F. Federici, G. de Cesare, D. Puglisi, and D. Caputo, "Gold Nanoparticles-Functionalized Cotton as Promising Flexible and Green Substrate for Impedometric VOC Detection", *Materials*, 16(17), 5826, 2023, doi: 10.3390/ma16175826

[26] S. Casalinuovo, A.Buzzin, D.Caschera, S.Quaranta, F.Federici, D.Puglisi, G.de Cesare, and D.Caputo, "Enhancing breath analysis with a novel AuNP-coated cotton sensor", *IEEE,* pp. 241-245, 2023, June, In 2023 9th International Workshop on Advances in Sensors and Interfaces (IWASI), doi: 10.1109/IWASI58316.2023.10164472

[27] E. Fraschetti, D. Puglisi, G. Domènech-Gil, A. Buzzin, A. Mastrandrea, I. Mazzetta, G. de Cesare, S. Casalinuovo, S. Quaranta, D.Caputo, "Characterization of Disposable Facemasks for COVID-19 Through Colorimetric Analysis", NanoInnovation 2021, doi: 10.1088/1757-899X/1265/1/012008

[28] S. Rab, M. Javaid, A. Haleem, and R. Vaishya, "Face masks are new normal after COVID-19 pandemic.", *Diabetes & Metabolic Syndrome,* vol. 14, pp. 1617-1619, 2020, doi: 10.1016/j.dsx.2020.08.021

[29] A. Buzzin, G. Domènech-Gil, E. Fraschetti, E. Giovine, D. Puglisi, D. Caputo, "Assessing the consequences of prolonged usage of disposable face masks.", *Scientific Reports,* vol. 12(1) pp 1-9, 2022, doi: 10.1038/s41598-022-20692-9

[30] S. Casalinuovo, A. Buzzin, A. Mastrandrea, I. Mazzetta, M. Barbirotta, L. Iannascoli, A. Nascetti, G. de Cesare, D. Puglisi, and D. Caputo, "3D-Printed Face Mask with Integrated Sensors as Protective and Monitoring Tool", AISEM, 2022, doi: 10.1007/978-3-031-25706-3_7

[31] S. Casalinuovo, A. Buzzin, M. Barbirotta, A.Mastrandrea, D. Puglisi, G. de Cesare, and D.Caputo, "Measurements of Exhaled CO2 Through a Novel Telemedicine Tool", *Cham: Springer Nature Switzerland,* pp. 396-401, 2023, September, In Annual Meeting of the Italian Electronics Society.

[32] D. Caschera, F. Federici, D. Zane, F. Focanti, A. Curulli, G. Padeletti, "Gold nanoparticles modified GC electrodes: Electrochemical behaviour dependence of different neurotransmitters and molecules

of biological interest on the particles size and shape.", *Journal of Nanoparticle Research,* vol. 11(8), pp. 1925-1936, 2009, doi: 10.1007/s11051-008-9547-0

[33] A. L. Soares, M. L. Zamora, L. F. Marchesi, and M. Vidotti, "Adsorption of catechol onto PEDOT films doped with gold nanoparticles: Electrochemical and spectroscopic studies." *Electrochimica Acta*, 322, p 134773, 2019, doi: 10.1016/j.electacta.2019.134773