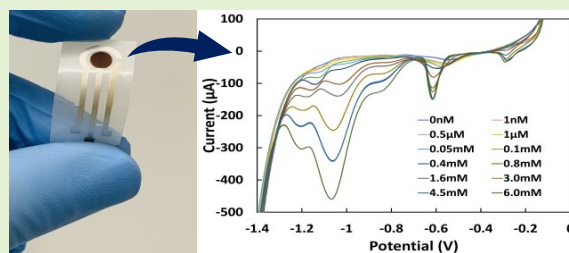


# Flexible screen-printed amperometric sensors functionalized with spray-coated carbon nanotubes and electrodeposited Cu nanoclusters for nitrate detection

A K M Sarwar Inam, Martina Aurora Costa Angeli, *Member, IEEE*, Bajramshahe Shkodra, Ali Douaki, Enrico Avancini, *Member, IEEE*, Luca Magagnin., *Member, IEEE*, Luisa Petti, *Member, IEEE* and Paolo Lugli, *Fellow, IEEE*

**Abstract**—In this work, we present a novel, sensitive, easy-to-fabricate, flexible amperometric sensor constituted by screen-printed silver (Ag) electrodes functionalized with a copper (Cu) film electrodeposited on top of a spray coated network of single-walled carbon nanotubes (SWCNTs). The Cu/SWCNTs/Ag electrode showed excellent catalytic activity towards the electro-reduction of nitrate ions at neutral pH with a significant increase in cathodic peak currents in comparison with the electrode without SWCNTs (Cu/Ag). The developed Cu/SWCNTs/Ag sensor showed a wide linear detection range from 0.5  $\mu\text{M}$  to 6.0 mM (0.31 mg/l to 372.02 mg/l) with good sensitivity (18.39  $\mu\text{A}/\text{mM}$ ) and a calculated limit of detection (LOD) of 0.166 nM (10.29  $\mu\text{g}/\text{l}$ ). It also showed a good selectivity (maximum standard deviation (SD) was 3.25  $\mu\text{A}$ ) towards different interfering ions ( $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$  and  $\text{HCO}_3^-$ ), as well as good reproducibility, mechanical durability, time and temperature stability. In real sample analysis (tap and river water), the sensor exhibited good agreement with the compared outcome of high-performance liquid chromatography (HPLC) measurements, proving to be a promising analytical tool for the detection of nitrate in water.

**Index Terms**—SWCNTs, electrochemical, nitrate sensor, flexible substrate, copper electrodeposition, screen printing



## I. INTRODUCTION

PURE drinking water is becoming one of the major assets all over the world, especially considering the constantly growing population. A major threat to the availability of pure water is given by the industrial and agricultural sectors, which lead to water contamination [1]. Nitrate ( $\text{NO}_3^-$ ) ions are among the main contaminants in water. In fact,  $\text{NO}_3^-$  is widely used not only as a food preservative to prevent poisoning from *Clostridium botulinum* in the industrial sector, but also as an additive to enhance the food color and flavor or as fertilizer in the agriculture [2], [3]. Despite these useful

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A K M Sarwar Inam, Martina Aurora Costa Angeli, Bajramshahe Shkodra, Ali Douaki, Enrico Avancini, Luisa Petti and Paolo Lugli are with the Sensing Technologies Lab, Faculty of Science and Technology, Free University of Bolzano, Bolzano, Italy (email: MCostaAngeli@unibz.it).

A K M Sarwar Inam is also with the Department of Nutrition and Food Engineering, Daffodil International University, Dhaka, Bangladesh

Luca Magagnin is with the Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Milano, Italy

applications, exposure to a high level of nitrate can put humans at risk of several chronic and acute conditions such as liver disease, gastric cancer, Parkinson disease, and blue-baby syndromes [4], [5]. Indeed,  $\text{NO}_3^-$  ions can lead to the formation of various harmful nitrogenous substances, such as nitrite, nitric oxide, N-nitrosamines [6]. Considering these toxic effects, the World Health Organization (WHO) as well as the European Directives have fixed the maximum contaminant level (MCL) of  $\text{NO}_3^-$  as 50 mg per liter (ca. 0.8 mM) in pure drinking water [7]. As a result, rapid and cost-effective methods able to detect nitrate content in drinking water are extremely required. In this context, electrochemical sensors have been widely investigated in nitrate monitoring because of their high sensitivity, selectivity, quick response, portability, and miniaturization [8]–[10]. Various electrochemical sensors such as amperometric, potentiometric, conductometric have been exploited to detect nitrate with or without the involvement of specific bio-recognition elements, such as enzymes [11]–[14]. In fact, different types of metals such as copper (Cu), platinum (Pt), silver (Ag) and gold (Au) have been utilized as catalysts for the reduction of nitrate eliminating the need for a specific bio-recognition element which complicates the

sensor fabrication and decreases the sensor shelf-life [15]–[17]. Among these electrocatalytic metals, Cu is surely the most effective metal to electro-reduce nitrate ions because of its high conductivity ( $58.14 \times 10^6$  S/m), improved charge transfer and cost-effectiveness [6], [18]–[20]. Recently, it has been shown that it is possible to reduce the limit of detection (LOD) of electrochemical nitrate sensors by increasing the electroactive surface area thanks to the use of nano composites made, for example, of Cu nanoparticles and carbon nanotubes or reduced graphene oxides [11], [21]. Single-walled carbon nanotubes (SWCNTs) have received considerable interest for electrochemical sensors due to their fast electron transfer, high conductivity (10,200 S/m) [22] and the ability to donate or receive electrons in a wide range of electrochemical potential, which allows them to be used as mediators in sensing platforms [23]. Moreover, because of their large area-to-volume ratio, SWCNTs allow enhancing the sensor sensitivity to the nanoscale response by increasing the electroactive surface area [24], [25].

Here, we demonstrate a novel, flexible, screen-printed amperometric electrochemical nitrate sensor, where SWCNTs are sprayed on an Ag working electrode, followed by the electrodeposition of Cu (Cu/SWCNTs/Ag sensor). With respect to the previous conference proceeding (IEEE FLEPS 2021), here we additionally presented a full characterization of the proposed sensors in terms of stability, selectivity towards different common based ions in drinking water, temperature of operation and real sample testing, which show evidence of the performance of the sensor regarding the novel aspects. The uniqueness of this proposed sensor is the combination of cost-effective and scalable techniques such as screen-printing, spray deposition of SWCNTs and electrodeposition of Cu in an easy and reliable method, if compared to previously reported papers [11], [26]. We also demonstrated that the presence of SWCNTs actively helps to increase the electroactive surface area successfully electro-reducing nitrate ions. The Cu/SWCNTs/Ag sensor is highly capable of detecting nitrate in water with a low calculated LOD (0.166 nM) and a wide linear detection range (0.5  $\mu$ M to 6 mM) by using linear sweep voltammetry (LSV). The most common interferents ( $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$  and  $\text{HCO}_3^-$ ) were studied and found very negligible effect on nitrate detection. The sensor was also tested for temperature dependency, repeatability, reproducibility, and stability in time. In the end, the sensor was tested with real water samples which showed a good agreement with HPLC results.

## II. METHODS

### A. Chemicals and apparatus

All chemicals and reagents (analytical grade) were used without further purification. Double distilled water (resistivity 18.2 M $\Omega$ .cm) was used in all solutions. Ferrous sulfate ( $\text{FeSO}_4$ ), sodium chloride (NaCl), potassium chloride (KCl), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium acetate ( $\text{CH}_3\text{COONa}$ ), sodium nitrate ( $\text{NaNO}_3$ ), and sodium nitrite ( $\text{NaNO}_2$ ) were purchased from Merck KGaA (Germany). 125  $\mu$ m thick polyethylene terephthalate (PET) was

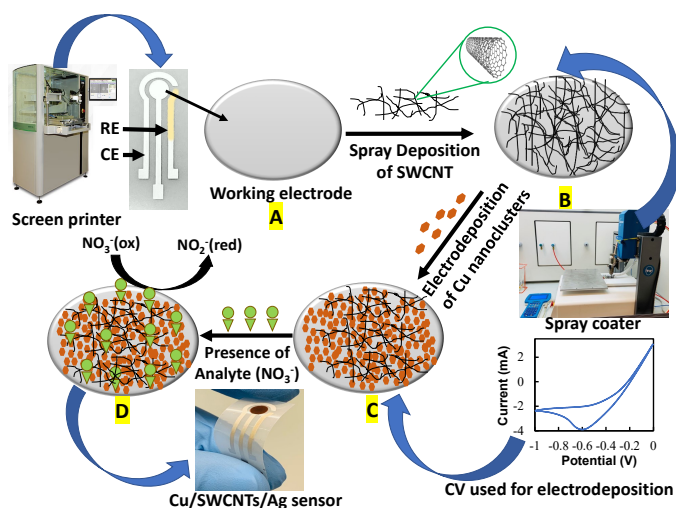


Fig. 1. Schematic illustration of the fabrication process of the proposed nitrate sensor consists of three electrodes system; working electrode (WE), counter electrode (CE) and reference electrode (RE): A) the screen-printed silver WE, B) modified with spray deposited single-walled carbon nanotubes (SWCNTs), C) further modified by electrodeposition of Cu, D) Reduction of nitrate in presence of the analyte.

used as a substrate (Rauch GmbH, Germany). To fabricate the electrodes Ag (ECI 1011) and AgCl (ECI 6038E) screen printed pastes were purchased from LOCTITE E&C (CA, USA). To electrodeposit Cu, 0.1 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (pH adjusted to 2.0) was used and 0.1 M KCl was used as an electrolyte in all the experiments. River water was collected from the Talvera River in Bolzano, Italy, and tap water was collected from the lab (city water supply in Bolzano, Italy). All electrochemical measurements were performed by using VersaSTAT 4 electrochemical workstation (Princeton Applied Research, USA) at room temperature. A 1525 Waters HPLC system (Waters Corporations, MA, USA) equipped with a Symmetry C18 Column (2.1  $\times$  50 mm, 3.5  $\mu$ m) and a photodiode array detection (PDA 2998) set at 286 nm was used.

### B. Sensor fabrication

The typical three-electrode electrochemical sensor structure was realized on top of a PET substrate with the use of a semi-automatic screen-printing machine (Aurel automation S.P.A. C290, Italy). The sensor structure consists of an Ag working electrode (WE) (diameter: 4mm) (Fig. 1A), an Ag counter electrode (CE) and an Ag/AgCl pseudo-reference electrode (RE). On top of the WE electrode, a water-based SWCNT dispersion prepared by the method of [27], was spray coated as described in [28] (Fig. 1B). Afterwards, Cu electrodeposition was performed on top of SWCNTs coated WE according to [29] (using CV at the potential range of  $-1.0$  to  $0$  V with a scan rate of  $0.1$  Vs $^{-1}$ ) in  $0.1$  M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{H}_2\text{SO}_4$  (pH = 2.0) solution at room temperature (Fig. 1C). Finally, the electrodes were slowly rinsed with double-distilled water.

### C. Morphological and compositional characterization

To analyze the surface morphology of the Cu/SWCNTs/Ag sensor and the crystal structure of electrodeposited Cu, scanning electron microscopy (SEM, Quanta 600F, FEI, USA),

atomic force microscope (AFM, CoreAFM, Nanosurf, Sweden), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS) were carried out. AFM was operated in static force mode with the 20nN of force setpoint having silicon AFM probes (ContAl-G) and a resonant frequency of 13 kHz. XRD patterns were measured by using an Ital Structures IPD3000 unit, Cu K $\alpha$  source, and multilayer monochromator at an incident angle on the sample of 5°. Powder patterns were acquired by means of a Dectris Mythen detector (1280 channels) over 10-130° 2-theta range with a 0.02° angular resolution and a total acquisition time of 2400 seconds for each sample. For EDS spectra, 30 s acquisition time and 20 kV acceleration voltage were used. The thickness and roughness of the sensor were measured using a Dektak 150 Surface Profiler (Veeco, NY, USA).

#### D. Electrochemical and mechanical measurements

To evaluate the electrode reaction mechanism and to calculate the active surface area, cyclic voltammetry (CV) was applied (potential range from -0.1 V to -1.4 V) with different scan rates (25 to 500 mVs<sup>-1</sup>) using 3.0 mM of NaNO<sub>3</sub> in 0.1 M KCl electrolyte solution. For the other characterizations, LSV over CV was chosen as measuring method because LSV identifies clearer nitrate reduction peak current [30]. LSV was performed in the potential range of -0.1 to -1.4 V with a scan rate of 10 mV s<sup>-1</sup> on different concentrations of NO<sub>3</sub><sup>-</sup>. To evaluate the effect of the temperature on the behavior of the sensor, it was tested changing the electrolyte temperature from 15 to 35 °C. Additionally, a customized bending setup was used to study the mechanical stability of the proposed sensor that was cyclically bent to a radius of 5 mm up to 1000 cycles.

### III. RESULTS AND DISCUSSION

#### A. Surface characterization

Fig. 2 shows the SEM image of the uniformly distributed Cu nanoclusters on top of the spray coated SWCNTs. From the image, it is easily noticeable that SWCNTs are uniformly

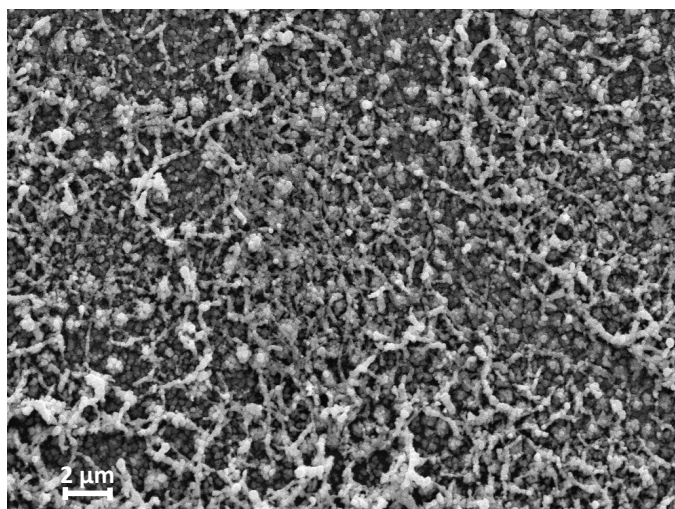


Fig. 2. Scanning electron microscopy (SEM) micrograph of electrodeposited Cu nanoclusters on top of SWCNTs coated Ag electrode.

covered by globular-shaped Cu nanoclusters. The diameter of a single Cu nanoparticle is homogeneous all over the WE in a range of 200 nm to 500 nm [31]. The SEM images from Fig. S1A show the bare Ag electrode, where the Ag flakes are clearly visible. The surface morphology is changed after SWCNT and Cu deposition (Fig. S1B). As shown in the AFM image in Fig. S2 (done by spraying 100 layers of SWCNTs on top of glass slide) the nanotubes are uniformly distributed on the substrate. XRD was measured at each step of the sensor fabrication to further investigate the outcome of the subsequent deposition processes for the different materials. Fig. 3 shows XRD patterns of the Ag WE electrode, SWCNTs/Ag WE electrode, and Cu/SWCNTs/Ag WE electrode. All the XRD patterns show peaks at Bragg reflections of crystalline Ag (111), (200), and (220). After the Cu electrodeposition process, the (111), (200) and (220) reflections of crystalline Cu, respectively observed at 43.7°, 50.9° and 74.7°, confirm the presence of crystalline Cu. This observation is in agreement to those previously found also by Chen et al [2]. The presence of Cu is also indicated by an EDS and another XRD measurements (Fig. S3 and S4). The EDS results (Fig. S3) show a normalized mass of 55.23% for Cu, 32.99% for C and 11.78% for O, consistent values with the multi-layers fabrication process. Whereas XRD results clearly indicate the presence of crystalline Cu after Cu electrodeposition, features of SWCNTs are not easily distinguishable on the XRD patterns of the samples where they are expected. This is likely because of the relatively small amount of SWCNTs material deposited on the surface as compared with Ag and Cu, and of the limits given by the S/N ratio. Additionally, the thickness and roughness results measured by using a surface profilometer demonstrated an increment from  $2.34 \pm 0.04 \mu\text{m}$  to  $3.26 \pm 0.03 \mu\text{m}$  and from  $0.80 \pm 0.01$  to  $1.00 \pm 0.20 \mu\text{m}$ , respectively, before and after SWCNTs and Cu deposition for the Cu/SWCNTs/Ag sensors. This observation has a good agreement with the SEM images (Fig. 2), demonstrating that the surface area increased by Cu

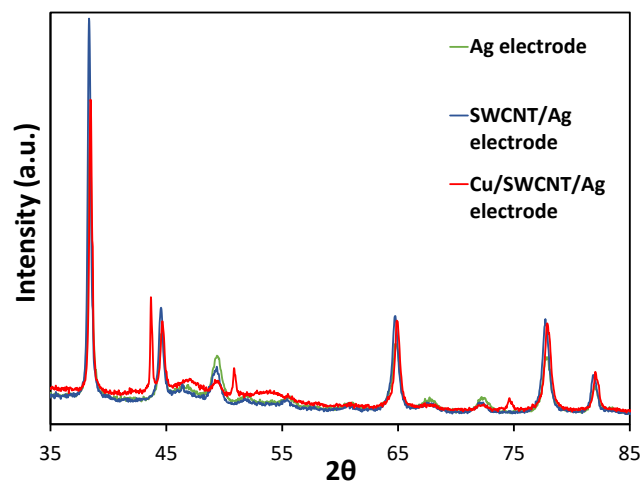


Fig. 3. A comparison of XRD patterns on different fabrication steps of the working electrode (Ag WE (green), SWCNTs/Ag WE (blue), and Cu/SWCNTs/Ag WE (red)).

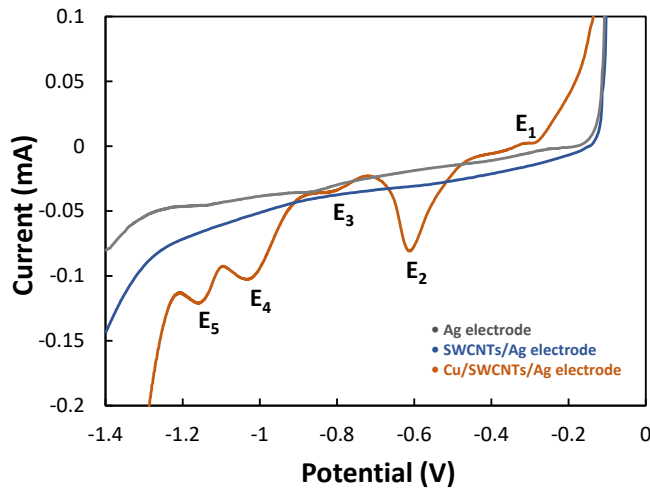
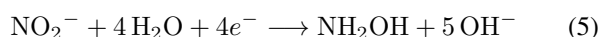
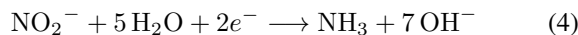
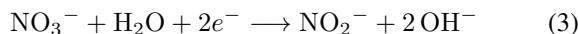
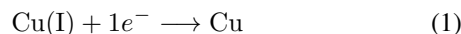


Fig. 4. Linear sweep voltammetry (LSV) analysis showing cathodic reduction peak current of Ag (ash), SWCNTs/Ag (blue) and Cu/SWCNTs/Ag (orange) electrode in the presence of 0.8 mM of  $\text{NO}_3^-$  concentration.

electrodeposition.

### B. Electrochemical characterization

Fig. 4 shows three different LSV performed to investigate the voltametric response of the reduction peak current of nitrate (0.8 mM in 0.1 M KCl) at each step of the sensor fabrication. The results show no response of nitrate reduction for both Ag and SWCNTs/Ag electrodes. Instead, the Cu/SWCNTs/Ag electrode (orange curve) shows 5 different cathodic reduction peaks. The peaks at -0.2 V and -0.6 V are attributed to the Cu (I) ( $E_1$ ) and Cu (II) ( $E_2$ ) reduction, respectively shown in Equations 1 and 2. At negative potentials,  $\text{NO}_3^-$  was reduced to  $\text{NO}_2^-$  ( $E_3$ ),  $\text{NO}_2^-$  was reduced to  $\text{NH}_3$  ( $E_4$ ) and in neutral or alkaline electrolyte concentration  $\text{NO}_2^-$  can be further reduced to  $\text{NH}_2\text{OH}$  ( $E_5$ ). These consecutive reaction shows three reduction peak at -0.8 V, -1 V and -1.15 V, respectively as similarly reported also in [32], [33]. Indeed, the primary product of  $\text{NO}_3^-$  reduction was  $\text{NO}_2^-$  which again is reduced to  $\text{NH}_3$  as showed in the equation 3 and 4 and also verified by Hasnat et al. [34] and Lotfi et al. [35]. From this observation it can be said that despite the possibility of Cu to form  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , it does not interfere with the sensing mechanism for nitrate reduction.



As the fabrication process involves a procedure of electrodeposition of Cu by CV, it is relevant to investigate the influence of the performed number of CV cycles on the sensor performance [31]. Therefore, electrodes realized by

using 4 different CV cycles (1, 2, 4 and 6) of Cu deposition on top of SWCNTs coated WE were measured in terms of current reduction peak at different nitrate concentrations (0, 0.1, 0.8, and 1.6 mM) (Fig. S5). The results (Fig. 5) show that the electrode realized using 2 CV cycles has the highest sensitivity and also the highest nitrate peak current reduction (Fig. S6). More than 2 CV cycles cause excess Cu nanoclusters deposition which may decrease the surface area because of reduction of the porosity by hiding the CNTs of the electrode. Therefore, 2 CV cycle was used as optimized electrodeposition of Cu to fabricate the sensor.

To investigate the nature of the electrochemical reaction of Cu/SWCNTs/Ag electrodes in presence of  $\text{NO}_3^-$ , the effect of the scan rate on the reduction peak current was studied in the set of measurements. Plotting the reduction peak current versus the square root of scan rate ( $v$ ) shown in Fig. S7, a linear correlation ( $R^2 = 0.969$ ) was observed suggesting that a diffusion-controlled process is taking place [40]. Additionally, the electrochemical active surface areas of both Cu/Ag (Cu was electrodeposited on screen printed Ag using 2 CV cycles) and Cu/SWCNTs/Ag was determined using the Randles-Sevcik equation [41] for comparison. It has been found that the effective surface areas of Cu/SWCNTs/Ag and Cu/Ag sensors were  $0.082 \text{ cm}^2$  and  $0.042 \text{ cm}^2$ , respectively, proving that the incorporation of SWCNTs can increase the surface area by up to 95.5% [42].

### C. Sensor performance for nitrate detection

To investigate the sensor performance, different concentrations (0 nM, 1 nM, 0.5  $\mu\text{M}$ , 1  $\mu\text{M}$ , 0.05mM, 0.1 mM, 0.4 mM, 0.8 mM, 1.6 mM, 3.0 mM, 4.5 mM, and 6.0 mM) of  $\text{NO}_3^-$  were tested by LSV at optimized experimental conditions for Cu/SWCNTs/Ag sensor (Fig. S8). The calibration curve (Fig. 6) plotted by averaging the nitrate reduction peak current of 3 samples for each concentration, shows a wide linear range from 0.5  $\mu\text{M}$  to 6.0 mM (1 nM was not considered

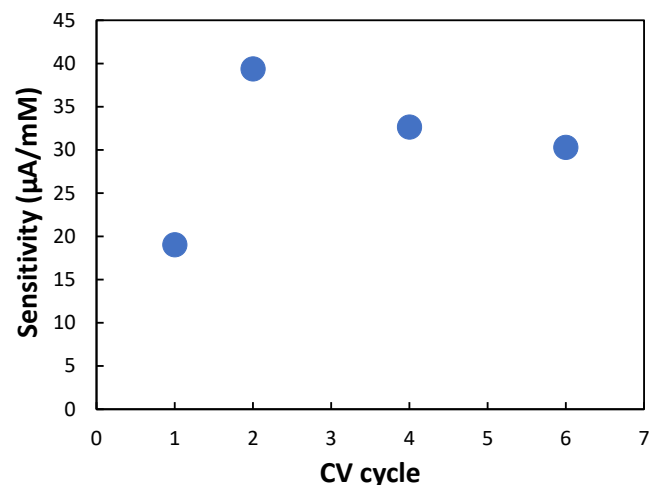


Fig. 5. Sensitivity (obtained using 4 different concentrations (0, 0.1, 0.8 and 1.6 mM of  $\text{NO}_3^-$ ) for different sensors which were prepared through different number of cyclic voltammetry (CV) cycles.

TABLE I

COMPARISON BETWEEN THE PERFORMANCE OF DIFFERENT NITRATE SENSOR WHERE CARBON NANOTUBES WERE INCORPORATED WITH OR WITHOUT THE PRESENCE OF CU NANOCLUSTERS.

Electrode modification	Method	Linear range (mM)	Sensitivity ( $\mu A/mM$ )	LOD (nM)	Ref.
Cu/MWCNT/RGO/GCE	SWV	0.001 – 0.075	$21.52 \times 10^3$	20	[11]
CNT/PPy/NR/GCE	CV	0.44 – 1.45	0.3	17	[22]
MWCNT/CuNPs/Ag-probe	LSV	0.001 - 5	80.62	0.333	[36]
CuNps/MWCNT-PEI/PPy-PSS/GCE	Am	0.1 - 5	137	$3 \times 10^4$	[37]
CuO/MWCNT/GCE	DPV	0.01 - 0.7	-	-	[38]
L-MWCNT/GCE	CV	0.5 - 10	-	900	[39]
Cu/SWCNT/SPSE	LSV	$5 \times 10^{-4}$ - 6	18.39	0.166	This work

Cu: Copper, MWCNT: Multi-walled carbon nanotubes, RGO: Reduced graphene oxide, GCE: Glassy carbon electrode, CNT: carbon nanotubes, NR: Nitrate reductase, CuNPs: Copper nanoparticles, PEI: Polyethyleneimine, PPy: Polypyrrole, PSS: Polystyrene sulfonate, L-MWCNT: Lipophilic multi-walled carbon nanotubes, SPSE: Screen-printed silver electrode, SWV: Square wave voltammetry, CV: Cyclic voltammetry, LSV: Linear sweep voltammetry, Am: Amperometry, DPV: Differential pulse voltammetry.

due to the high SD value), with good repeatability and reproducibility (SD ranges from 0.91 to 5.14  $\mu A$ ). As expected, the Cu/SWCNTs/Ag sensor showed excellent sensitivity (18.39  $\mu A/mM$ ) with a high coefficient of determination (99.72%). This sensor showed higher sensitivity comparing to Cu/Ag sensor (sensitivity (12.19  $\mu A/mM$  with  $R^2 = 0.98$ ). To calculate the detection limit, the following equation was used:

$$LOD = (3.3STDEVI_0)/m \quad (6)$$

where  $I_0$  is the generated peak current at 0 mM  $NO_3^-$  and  $m$  is the slope of the linear response curve.

The LOD was found to be 0.166 nM for Cu/SWCNTs/Ag sensor comparing to Cu/Ag sensor (LOD 0.381 nM) [42], which indicates that the incorporation of SWCNTs increased the electron transfer kinetics, possibly thanks to the increase of the electroactive surface area. While comparing the calculated LOD as well as the linear detection range of this sensor with other nitrate sensors where carbon nanotubes were incorporated with or without various forms of Cu (Table I), it can

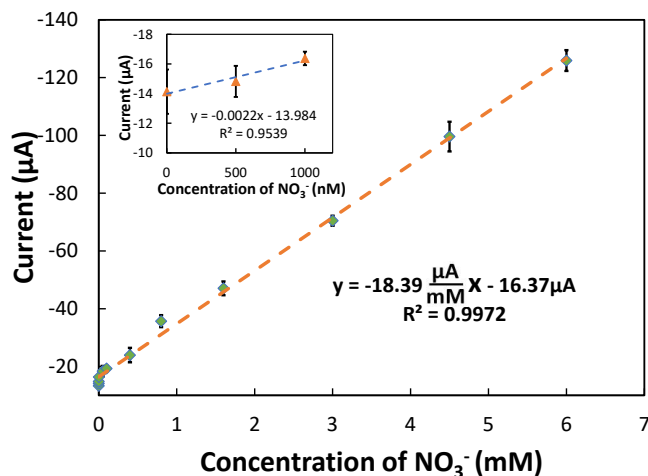


Fig. 6. Calibration curve of Cu/SWCNTs/Ag sensor for nitrate detection ( $NO_3^-$  reduction peak current versus  $NO_3^-$  concentration). Inset shows the lowest concentration (1nM, 500nM and 1000 nM). Each point is the average peak current performed by 3 electrodes, where the standard deviation with error bars is shown.

be found that the obtained LOD was lower, with a wider range of detection. This is probably due to the covering of SWCNTs by electrodeposited Cu, providing straight conducting pathways for electron transfer and higher surface area with outstanding adsorption property [33]. Moreover, these results were obtained using a neutral electrolyte solution (0.1 M KCl) showing the ability to measure nitrate ions in real water sample without the need of pH control, whereas for most of the proposed sensors an acidic medium ( $Na_2SO_4$ , pH 2.0) was used as electrolyte [11], [26], [43].

#### D. Effect of temperature

The effect of temperature on the sensor performance is one relevant factor that has to be evaluated as it can change the performance of the sensors and the kinetics of the electrochemical reaction. The temperature effect was investigated between 15 to 35°C by testing the Cu/SWCNTs/Ag electrode at 0.8 mM of  $NO_3^-$  using 3 sensors for each tested temperature. The results (Fig.7) show that the reduction peak current is stable till 25°C and later it starts to increase with temperature showing a 6.5% and 13% variation at 30 and 35°C, respectively, if compared

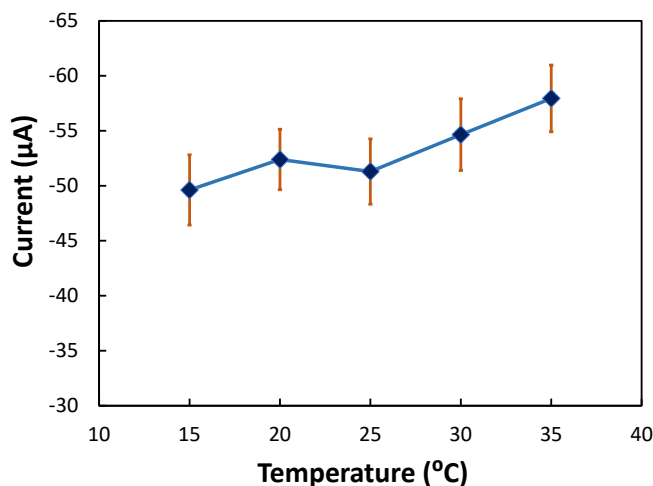


Fig. 7. The effect of temperature analysis in 5 different temperature (15, 20, 25, 30, and 35 °C) using 0.8 mM of  $NO_3^-$ .

to 25°C. This behaviour can be ascribed to the increase of the reaction rate with increasing temperature as reported by [44] and it can be compensated with the integration of a temperature sensor.

### E. Selectivity and reproducibility

Since the objective of this proposed sensor is to detect nitrate in real water, it is important to evaluate if the anions and cations ( $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$  and  $\text{HCO}_3^-$ ), commonly found in water, can interfere with the sensor performance [11], [15], [18], [43], [45]. Thus, 0.8 mM concentration of the above-mentioned interfering agents were prepared and tested for nitrate reduction peak current (at -0.85 V) and compared with the blank solution (0 mM of  $\text{NO}_3^-$  in 0.1 M KCl). The results are summarized in Fig. S9. The amplitudes of the current at -0.85 V for all the tested ions are similar to the blank concentration with a small variation which can be ascribed to experimental error, demonstrating the high selectivity of the proposed Cu/SWCNTs/Ag sensor. Additionally, to check if these interfering agents co-interfere with nitrate, all these chemicals were prepared at 0.8 mM with the presence of also 0.8 mM of  $\text{NO}_3^-$ . Results are summarized in Fig. 8, where the variation of the reduction peaks of  $\text{NO}_3^-$  at -0.85 V are shown.  $\text{Cl}^-$  ions showed the highest reduction peak current if compared to the other interferents. This is commonly reported also in the literature [46], [47] as there is the possibility of the formation of  $\text{CuCl}_2$  on top of the WE in presence of  $\text{Cl}^-$  ions which increase the reduction current [48]. In general, the effects of the interferents are minor and thus the proposed sensor can be selectively used in real water containing these possible interferents.

Reproducibility of the proposed sensors is another important aspect to evaluate. Therefore, 5 different concentrations of nitrate (0.1, 0.8, 1.6, 3.0, and 6.0 mM) were tested using three sensors from different batches. Standard deviation (SD) was calculated and found to be 0.73  $\mu\text{A}$ , 1.87  $\mu\text{A}$ , 2.28  $\mu\text{A}$ , 3.23  $\mu\text{A}$  and 4.99  $\mu\text{A}$ , respectively. The results proved that the sensors, which go through different fabrication steps such as screen-printing, SWCNT spray deposition and Cu electrodeposition, maintained a good reproducibility.

### F. Regeneration and stability

To evaluate the regeneration of the sensor, a repeatability analysis was performed. The same sensor was examined consecutively 9 times with 0.8 mM of  $\text{NO}_3^-$  and reduction peak current was measured (Fig. S10). Each time after the measurement, the electrode was washed with DI water, dried with compressed air to make ready for the next. 3 electrodes were used for this test and results are shown in figure with error bars (SD). The results indicate that the same sensor is usable only two times, as the current decreases by 4.7% at the 2nd measurement and by 17.6% in the 3rd. The possible explanation for this change of current is the delamination of carbon nanotubes while rinsing the sensor with DI water and also the continuous applied potential that can degenerate the pseudo-reference electrode [49]. Nonetheless, this is acceptable finding because the proposed device is meant to be one-time usable and disposable.

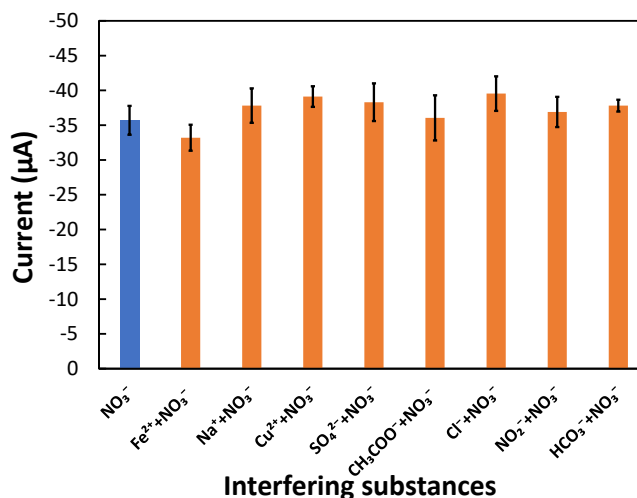


Fig. 8. Interference analysis using reduction peak current in the presence of 0.8 mM  $\text{NO}_3^-$  and 0.8 mM of  $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ , and  $\text{HCO}_3^-$  respectively.

To determine the shelf life, sensor stability was tested by measuring nitrate reduction peak current every week up to one month. A total of 15 sensors were prepared in the same batch and kept at room temperature (around 22°C). Every week, three sensors were tested in the previously mentioned 0.8 mM nitrate solution by measuring the nitrate reduction peak current. The average results with error bars from SD values are plotted in Fig. 9. The reduction peak currents did not show a sharp change but reduced gradually after every week with a slow increment of the SD value. Since the SD value of reduction peak current at 0.8 mM of  $\text{NO}_3^-$  concentration in the calibration curve showed 2.08  $\mu\text{A}$  of deviation and in the 2nd week of stability test the SD value showed 2.45  $\mu\text{A}$  of deviation, it can be evinced that the sensor performance is stable for the first two weeks only. The reason for this fluctuation of the reduction peak current could be related to the formation of oxidative layers on top of the Cu layer in the

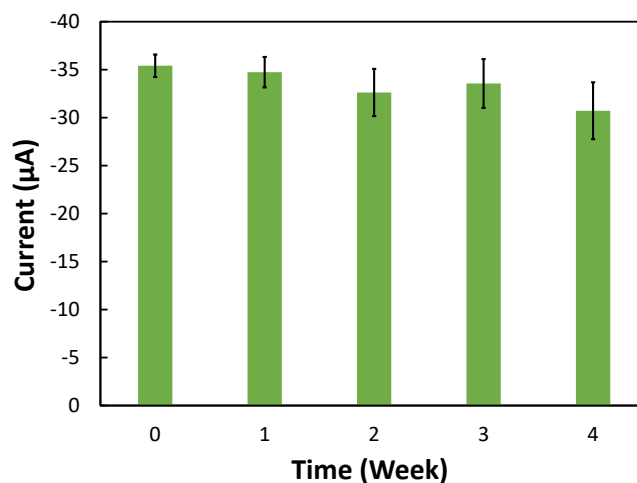


Fig. 9. Stability test for a month for Cu/SWCNTs/Ag sensor shows the reduction peak (average of 3 samples) of 0.8 mM  $\text{NO}_3^-$  repeated each week until 1 month.

TABLE II  
NITRATE DETECTION IN DIFFERENT WATER SAMPLES

Parameters	Tap water	River water
Added NO <sub>3</sub> <sup>-</sup> (mM)	0.8	0.8
Detected by sensor (mM)	0.855 ± 0.037	0.883 ± 0.007
Relative recovery (%)	106.9	110
Detected by HPLC (mM)	0.858 ± 0.040	0.903 ± 0.028

working electrode, which could be minimized by preparing the sensor in a nitrogen atmosphere and by keeping it in airtight environment.

### G. Mechanical stability test

The sensors were bent to a radius of 5 mm to apply tensile strain in both the electrode interconnect and sensing part for 500 and 1000 bending cycles with the help of a customized bending setup (Fig. S11A) and the nitrate reduction peak current after each bending test was measured. As shown in Fig. S11B, the current generation was unchanged after such repetitive bending cycles, demonstrating the stability of the sensors to mechanical deformation [42]. Nevertheless, the SD for both the electrode and sensor bending conditions increased from ± 2.07 to ± 6.07 μA and ± 0.58 to ± 2.48 μA respectively, after 1000 bending cycles, suggesting the possible formation of permanent nano-cracks in the electrode or other structural defects.

### H. Real sample analysis

To validate the proposed sensor, it is fundamental to evaluate its performance using real water samples. Standard addition method (SAM) was applied here to get the accuracy in practical analysis with tap and river water [50] and finally compared the result with HPLC. By using this technique, no extra preparation or purification is needed and also it does not need the calibration lines as the matrix effect is taken into account [51]. The real sample was mixed with 0.8 mM of nitrate and experiments were performed in triplicate under identical conditions. The nitrate concentration of tap water and river water showing in Table II are 0.855 ± 0.037 and 0.883 ± 0.007, respectively using the standard addition method with a relative recovery (RR) of 106.9% and 110% with coefficient of variance of 4.36% and 0.79%, respectively. Previously, HPLC was calibrated ( $R^2 = 0.9988$ ) with a wide range of nitrate concentration (0.1 mM to 6 mM) using double distilled water. The real water sample consists of a solution with river or tap water as solvent and a known solution of nitrate (0.8 mM). The final nitrate concentrations was measured by HPLC, which allows this to be used as a standard for the validation of devices in different studies. The HPLC of this real-water reference solutions are reported in table II. The results of nitrate content from the tap and river water on HPLC showed a good correlation with the results from the proposed sensor. Hence, it can be said that the proposed Cu/SWCNT/Ag sensor has high accuracy and reliability for nitrate detection from real environment.

## IV. CONCLUSION

In this paper, a flexible, cost-effective, easy-to-fabricate Cu/SWCNTs/Ag screen-printed sensor was developed for nitrate detection in water. The incorporation of SWCNTs showed increased electron transfer kinetics by providing larger electroactive surface area (95.5% larger compared to Cu/Ag sensor). In an optimized condition, this proposed sensor can detect the nitrate from 0.5 μM to 6.0 mM with a LOD of 0.166 nM. Also, the sensor showed high reproducibility and low repeatability allowing to use same sensor only twice, which is normal for a disposable device. The stability test conducted over a month demonstrated that the sensor showed minimal change in performance within a 2-week shelf storage at ambient temperature and humidity. On the other hand, mechanical stability tests showed the sensor can easily handle at least 500 bending cycles with minimal performance alteration. Finally, to investigate if the sensor can measure the analyte of interest in a real water sample, the tests using river and tap water showed reliable performance. In future, the sensor can be improved by introducing different transducing platform, such as electrolyte-gated field-effect transistor (EGFET) to improve the sensitivity and by implementing it into a portable device.

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## REFERENCES

- [1] M. H. Ward, R. R. Jones, J. D. Brender, T. M. de Kok, P. J. Weyer, B. T. Nolan, C. M. Villanueva, and S. G. van Breda, "Drinking water nitrate and human health: An updated review," *International Journal of Environmental Research and Public Health*, vol. 15, no. 7, pp. 1–31, 2018.
- [2] X. Chen, G. Zhou, S. Mao, and J. Chen, "Rapid detection of nutrients with electronic sensors: A review," *Environmental Science: Nano*, vol. 5, no. 4, pp. 837–862, 2018.
- [3] D. Reddy, J. Lancaster, and D. Cornforth, "Nitrite inhibition of Clostridium botulinum: electron spin resonance detection of iron-nitric oxide complexes," *Science*, vol. 221, no. 4612, pp. 769–770, aug 1983.
- [4] D. Brkić, J. Bošnjir, M. Bevardi, A. G. Bošković, S. Miloš, D. Lasić, A. Krivohlavek, A. Racz, A. M. Čuić, and N. U. Trstenjak, "Nitrate in leafy green vegetables and estimated intake," *African Journal of Traditional, Complementary and Alternative Medicines*, vol. 14, no. 3, pp. 31–41, 2017.
- [5] Y. H. Loh, P. Jakszyn, R. N. Luben, A. A. Mulligan, P. N. Mitrou, and K. T. Khaw, "N-nitroso compounds and cancer incidence: The European Prospective Investigation into Cancer and Nutrition (EPIC)-Norfolk Study," *American Journal of Clinical Nutrition*, vol. 93, no. 5, pp. 1053–1061, 2011.

- [6] G. E. Badea, "Electrocatalytic reduction of nitrate on copper electrode in alkaline solution," *Electrochimica Acta*, vol. 54, no. 3, pp. 996–1001, 2009.
- [7] S. Water and W. H. Organization, "": incorporating first addendum. Vol. 1, Recommendations," 2006. [Online]. Available: <http://apps.who.int/iris/handle/10665/43428>
- [8] C. Jiang, Y. He, and Y. Liu, "Recent advances in sensors for electrochemical analysis of nitrate in food and environmental matrices," *Analyst*, vol. 145, no. 16, pp. 5400–5413, 2020.
- [9] M. Kato, M. Okui, S. Taguchi, and I. Yagi, "Electrocatalytic nitrate reduction on well-defined surfaces of tin-modified platinum, palladium and platinum-palladium single crystalline electrodes in acidic and neutral media," *Journal of Electroanalytical Chemistry*, vol. 800, no. 2, pp. 46–53, sep 2017.
- [10] S. Mao, J. Chang, G. Zhou, and J. Chen, "Nanomaterial-enabled Rapid Detection of Water Contaminants," *Small*, vol. 11, no. 40, pp. 5336–5359, 2015.
- [11] H. Bagheri, A. Hajian, M. Rezaei, and A. Shirzadmehr, "Composite of Cu metal nanoparticles-multiwall carbon nanotubes-reduced graphene oxide as a novel and high performance platform of the electrochemical sensor for simultaneous determination of nitrite and nitrate," *Journal of Hazardous Materials*, vol. 324, pp. 762–772, 2017.
- [12] M. E. E. Alahi, A. Nag, S. C. Mukhopadhyay, and L. Burkitt, "A temperature-compensated graphene sensor for nitrate monitoring in real-time application," *Sensors and Actuators, A: Physical*, vol. 269, pp. 79–90, 2018.
- [13] D. Albanese, M. Di Matteo, and C. Alessio, *Screen printed biosensors for detection of nitrates in drinking water*. Elsevier B.V., 2010, vol. 28, no. C.
- [14] Y. Li, H. Li, Y. Song, H. Lu, J. Tong, C. Bian, J. Sun, and S. Xia, "An Electrochemical Sensor System with Renewable Copper Nano-Clusters Modified Electrode for Continuous Nitrate Determination," *IEEE Sensors Journal*, vol. 16, no. 24, pp. 8807–8814, 2016.
- [15] G. E. Dima, A. C. De Voosy, and M. T. Koper, "Electrocatalytic reduction of nitrate at low concentration on coinage and transition-metal electrodes in acid solutions," *Journal of Electroanalytical Chemistry*, vol. 554–555, no. 1, pp. 15–23, 2003.
- [16] M. H. Motaghehdifard, S. M. Pourmortazavi, M. Alibolandi, and S. Mirsadeghi, "Au-modified organic/inorganic MWCNT/Cu/PANI hybrid nanocomposite electrode for electrochemical determination of nitrate ions," *Microchimica Acta*, vol. 188, no. 3, p. 99, mar 2021.
- [17] J. Wang, Z. Zhang, and S. Wang, "Facile fabrication of Ag/GO/Ti electrode by one-step electrodeposition for the enhanced cathodic reduction of nitrate pollution," *Journal of Water Process Engineering*, vol. 40, no. November 2020, p. 101839, 2021.
- [18] J. Liang, Y. Zheng, and Z. Liu, "Nanowire-based Cu electrode as electrochemical sensor for detection of nitrate in water," *Sensors and Actuators, B: Chemical*, vol. 232, pp. 336–344, 2016.
- [19] E. Y. Frag, M. E.-B. Mohamed, and H. S. Salem, "Preparation and characterization of in situ carbon paste and screen-printed potentiometric sensors for determination of econazole nitrate: surface analysis using SEM and EDX," *Journal of the Iranian Chemical Society*, vol. 14, no. 11, pp. 2355–2365, nov 2017.
- [20] F. Amiripour, S. N. Azizi, and S. Ghasemi, "Nano P zeolite modified with Au/Cu bimetallic nanoparticles for enhanced hydrogen evolution reaction," *International Journal of Hydrogen Energy*, vol. 44, no. 2, pp. 605–617, 2019.
- [21] B. Hafezi and M. R. Majidi, "A sensitive and fast electrochemical sensor based on copper nanostructures for nitrate determination in foodstuffs and mineral waters," *Analytical Methods*, vol. 5, no. 14, pp. 3552–3556, 2013.
- [22] F. Can, S. Korkut Ozoner, P. Ergenekon, and E. Erhan, "Amperometric nitrate biosensor based on Carbon nanotube/Polypyrrole/Nitrate reductase biofilm electrode," *Materials Science and Engineering C*, vol. 32, no. 1, pp. 18–23, 2012.
- [23] S. Korkut, B. Keskinler, and E. Erhan, "An amperometric biosensor based on multiwalled carbon nanotube-poly(pyrrrole)-horseradish peroxidase nanobiocomposite film for determination of phenol derivatives," *Talanta*, vol. 76, no. 5, pp. 1147–1152, 2008.
- [24] Y. Yao and K. K. Shiu, "Electron-transfer properties of different carbon nanotube materials, and their use in glucose biosensors," *Analytical and Bioanalytical Chemistry*, vol. 387, no. 1, pp. 303–309, 2007.
- [25] W. Khan, S. Hussain, A. M. Siddiqui, and S. S. Islam, "Study of chemically functionalized carbon nanotubes," *AIP Conference Proceedings*, vol. 1536, pp. 199–200, 2013.
- [26] A. M. Stortini, L. M. Moretto, A. Mardegan, M. Ongaro, and P. Ugo, "Arrays of copper nanowire electrodes: Preparation, characterization and application as nitrate sensor," *Sensors and Actuators, B: Chemical*, vol. 207, no. Part A, pp. 186–192, 2015.
- [27] B. Shkodra, B. D. Abera, G. Cantarella, A. Douaki, E. Avancini, L. Petti, and P. Lugli, "Flexible and printed electrochemical immunosensor coated with oxygen plasma treated SWCNTs for histamine detection," *Biosensors*, vol. 10, no. 4, pp. 1–12, 2020.
- [28] B. D. Abera, A. Falco, P. Ibba, G. Cantarella, L. Petti, and P. Lugli, "Flexible Dispense-Printed Electrochemical Biosensor for Aflatoxin M1 Detection Employing NaOH and Oxygen Plasma Electrode Pretreatment," *FLEPS 2019 - IEEE International Conference on Flexible and Printable Sensors and Systems, Proceedings*, pp. 9–11, 2019.
- [29] Z. Mumtarin, M. M. Rahman, H. M. Marwani, and M. A. Hasnat, "Electro-kinetics of conversion of NO<sub>3</sub><sup>-</sup> into NO<sub>2</sub><sup>-</sup> and sensing of nitrate ions via reduction reactions at copper immobilized platinum surface in the neutral medium," *Electrochimica Acta*, vol. 346, p. 135994, jun 2020.
- [30] X. Wang, M. Zhu, G. Zeng, X. Liu, C. Fang, and C. Li, "A three-dimensional Cu nanobelt cathode for highly efficient electrocatalytic nitrate reduction," *Nanoscale*, vol. 12, no. 17, pp. 9385–9391, 2020.
- [31] Y. Li, J. Sun, C. Bian, J. Tong, H. Dong, H. Zhang, and S. Xia, "Copper nano-clusters prepared by one-step electrodeposition and its application on nitrate sensing," *AIP Advances*, vol. 5, no. 4, p. 041312, apr 2015.
- [32] Z. Mumtarin, M. M. Rahman, H. M. Marwani, and M. A. Hasnat, "Electro-kinetics of conversion of NO<sub>3</sub><sup>-</sup> into NO<sub>2</sub><sup>-</sup> and sensing of nitrate ions via reduction reactions at copper immobilized platinum surface in the neutral medium," *Electrochimica Acta*, vol. 346, p. 135994, 2020.
- [33] R. K. Amali, H. N. Lim, I. Ibrahim, N. M. Huang, Z. Zainal, and S. A. Ahmad, "Significance of nanomaterials in electrochemical sensors for nitrate detection: A review," *Trends in Environmental Analytical Chemistry*, vol. 31, no. June, p. e00135, 2021.
- [34] M. Hasnat, S. Ben Aoun, S. Nizam Uddin, M. Alam, P. Koay, S. Amertharaj, M. Rashed, M. M. Rahman, and N. Mohamed, "Copper-immobilized platinum electrocatalyst for the effective reduction of nitrate in a low conductive medium: Mechanism, adsorption thermodynamics and stability," *Applied Catalysis A: General*, vol. 478, pp. 259–266, may 2014.
- [35] H. R. Lotfi Zadeh Zhad and R. Y. Lai, "Comparison of nanostructured silver-modified silver and carbon ultramicroelectrodes for electrochemical detection of nitrate," *Analytica Chimica Acta*, vol. 892, pp. 153–159, 2015.
- [36] S. Parveen, A. Pathak, and B. D. Gupta, "Fiber optic SPR nanosensor based on synergistic effects of CNT/Cu-nanoparticles composite for ultratrace sensing of nitrate," *Sensors and Actuators, B: Chemical*, vol. 246, pp. 910–919, 2017.
- [37] E. Andreoli, V. Annibaldi, D. A. Rooney, K. S. Liao, N. J. Alley, S. A. Curran, and C. B. Breslin, "Electrochemical conversion of copper-based hierarchical micro/nanostructures to copper metal nanoparticles and their testing in nitrate sensing," *Electroanalysis*, vol. 23, no. 9, pp. 2164–2173, 2011.
- [38] D. Pan, W. Lu, S. Wu, H. Zhang, and W. Qin, "In situ spontaneous redox synthesis of carbon nanotubes/copper oxide nanocomposites and their preliminary application in electrocatalytic reduction of nitrate," *Materials Letters*, vol. 89, pp. 333–335, 2012.
- [39] M. Cuartero, G. Crespo, T. Cherubini, N. Pankratova, F. Confalonieri, F. Massa, M. L. Tercier-Waeber, M. Abdou, J. Schäfer, and E. Bakker, "In Situ Detection of Macronutrients and Chloride in Seawater by Submersible Electrochemical Sensors," *Analytical Chemistry*, vol. 90, no. 7, pp. 4702–4710, 2018.
- [40] B. Shkodra, A. Douaki, B. D. Abera, P. Ibba, E. Avancini, G. Cantarella, L. Petti, and P. Lugli, "A PEDOT:PSS/SWCNT-Coated Screen Printed Immunosensor for Histamine Detection in Food Samples," pp. 1–4, 2020.
- [41] A. Douaki, B. D. Abera, G. Cantarella, B. Shkodra, A. Mushtaq, P. Ibba, A. K. Inam, L. Petti, and P. Lugli, "Flexible screen printed aptasensor for rapid detection of furaneol: A comparison of CNTs and AgNPs effect on aptasensor performance," *Nanomaterials*, vol. 10, no. 6, pp. 1–18, 2020.
- [42] A. K. M. S. Inam, M. A. C. Angeli, B. Shkodra, A. Douaki, E. Avancini, L. Magagnin, L. Petti, and P. Lugli, "Flexible screen-printed nitrate sensors with Cu nanoclusters: a comparative analysis on the effect of carbon nanotubes," no. Cd, pp. 1–4, 2021.
- [43] B. Patella, R. R. Russo, A. O. Riordan, G. Aiello, C. Sunseri, and R. Inguanta, "Copper nanowire array as highly selective electrochemical sensor of nitrate ions in water," *Talanta*, vol. 221, no. September 2020, p. 121643, 2021.



- [44] S. J. Cho, S. Sasaki, K. Ikebukuro, and I. Karube, "A simple nitrate sensor system using titanium trichloride and an ammonium electrode," *Sensors and Actuators, B: Chemical*, vol. 85, no. 1-2, pp. 120–125, 2002.
- [45] I. S. Da Silva, W. R. De Araujo, T. R. Paixão, and L. Angnes, "Direct nitrate sensing in water using an array of copper-microelectrodes from flat flexible cables," *Sensors and Actuators, B: Chemical*, vol. 188, pp. 94–98, 2013.
- [46] J. Davis, M. J. Moorcroft, S. J. Wilkins, G. Compton, and M. F. Cardoso, "Electrochemical detection of nitrate and nitrite at a copper modified electrode," pp. 737–741, 2000.
- [47] N. G. Carpenter and D. Pletcher, "Amperometric method for the determination of nitrate in water," *Analytica Chimica Acta*, vol. 317, no. 1-3, pp. 287–293, 1995.
- [48] G. Karim-Nezhad and P. Seyed Dorraji, "Copper chloride modified copper electrode: Application to electrocatalytic oxidation of methanol," *Electrochimica Acta*, vol. 55, no. 9, pp. 3414–3420, 2010.
- [49] H. M. Mohamed, "Screen-printed disposable electrodes: Pharmaceutical applications and recent developments," *TrAC - Trends in Analytical Chemistry*, vol. 82, pp. 1–11, 2016.
- [50] M. Bader, "A systematic approach to standard addition methods in instrumental analysis," *Journal of Chemical Education*, vol. 57, no. 10, pp. 703–706, 1980.
- [51] J. E. Andersen, "The standard addition method revisited," *TrAC - Trends in Analytical Chemistry*, vol. 89, pp. 21–33, 2017.



**A K M Sarwar Inam** is currently in the Ph.D. program at the Sensing Technologies Lab of Free University of Bozen-Bolzano, Bolzano, Italy. He is working on the realization of electrochemical sensors for the food safety assessment. He was working as an Assistant Professor in the Department of Nutrition and Food Engineering, Daffodil International University, Bangladesh. He completed his Masters in Food Science, Technology and Nutrition from KU Leuven, Belgium (2012-2014) and Bachelor in Food Engineering from Bangladesh Agricultural University, Bangladesh (2007).



and human monitoring, and food safety.

**Martina Aurora Costa Angeli** received the master's degree in biomedical engineering (2016) from Politecnico di Milano (Italy), where she obtained the Ph.D. in materials engineering in 2020 working on the development of different types of deformable printed low-cost sensors for strain measurement. Currently, she is a post-doctoral researcher at the Sensing Technologies Lab of Free University of Bolzano (Italy). Her current research work is focusing on the design of low-cost flexible sensors for environmental



**Bajramshahe Shkodra** obtained the M.Sc. degree in the field of Analytical and Environmental Chemistry from the University of Prishtina, Kosovo (2017). Currently, she is a PhD student at the Free University of Bozen-Bolzano, working on the development of flexible and printed biosensors at the Sensing Technologies Lab. Her main research area includes the design, fabrication, and characterization of biosensors for food application.



ery to be implemented inside food packaging.

**Ali Douaki** received his B.Sc. and M.Sc. in Process Engineering from the University of Science and Technology Houari Boumediene (Algeria). Since November 2018 he is a PhD student at Free University of Bozen-Bolzano with a thesis entitled "Development of biodegradable smart packaging". Ali's work aims at the development and characterization of aptamers for sensing application, and the development of fully autonomous closed-loop systems for sensing, energy harvesting (through NFC), and drug delivery



degree in Physics (FU Berlin, 2014) and conducted his master thesis activities at Helmholtz-Zentrum Berlin (2013-2014). He holds a Bachelor's degree in Physics (University of Trento, 2012).

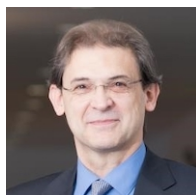
**Enrico Avancini** is a technologist since January 2020, working mainly on the management of laboratories. Prior to that, he conducted postdoctoral research (AR) at the Sensing Technologies Lab of Unibz, mainly working on nanotechnologies-based printed sensors. As a doctoral student (ETH Zurich, 2015-2019), he worked on the deposition and characterization of CIGS solar cells at Empa (Dübendorf, Switzerland), and obtained the title of Dr. sc. ETH Zurich in 2019. He holds a Master of Science (M.Sc.)



**Luca Magagnin** received the M.S. degree in nuclear engineering and the Ph.D. degree in electrochemical engineering from Politecnico di Milano, Italy. He was a Visiting Scientist at the University of California at Berkeley, in 2001, and a Visiting Professor with Keio University, Tokyo, in 2015. He is currently a Full Professor and head of the Surface and Electrochemical Engineering Laboratory at Politecnico di Milano. He has more than 200 publications (articles, patents, book chapters).



**Luisa Petti** received the M.Sc. degree in electronic engineering from the Politecnico di Milano, Milan, Italy, in 2011, and the Ph.D. degree in electrical engineering and information technology from ETH Zürich, Zürich, Switzerland, in 2016. She is currently an Associate Professor with the Free University of Bozen-Bolzano, Bolzano, Italy, where she researches on flexible and printed electronics for a wide range of applications, including food engineering and biotechnology.



**Paolo Lugli** graduated in physics from the University of Modena and Reggio Emilia, Italy, in 1979. He received the M.Sc. and Ph.D. degrees in electrical engineering from Colorado State University, Fort Collins, CO, USA, in 1982 and 1985, respectively. He is currently the Rector of the Free University of Bozen-Bolzano. He has authored more than 560 scientific articles.