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Flexible screen-printed nitrate sensors with Cu nanoclusters: a comparative analysis on the effect of carbon nanotubes

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***Abstract*— In this work, we present a novel flexible amperometric sensor for nitrate detection, based on a silver (Ag) working electrode modified with single-walled carbon nanotubes (SWCNTs) and copper (Cu). A simple and low-cost fabrication technique combining printing and electrochemical deposition was used: after spray deposition of SWCNTs on the screen-printed Ag working electrode, Cu was electrodeposited. The electrochemical performance of our sensors was analyzed and compared to reference sensors fabricated without SWCNTs (Cu/Ag), proving the capability of SWCNTs to improve the sensitivity and the performance of the sensors thanks to the increased electroactive surface area. In fact, the Cu/SWCNTs/Ag sensors showed higher catalytic activity towards the electro-reduction of nitrate (sensitivity: 18.19 µA/mM), as well as a lower limit of detection (LOD: 0.281 nM) in comparison to the Cu/Ag sensors (sensitivity: 12.19 µA/mM and LOD: 0.381 nM). Full sensor functionality after repetitive mechanical bending to 5 mm radius was also proven.**

Keywords*— *SWCNTs; amperometric; nitrate sensor; flexible substrate; copper electrodeposition.

I. Introduction

Nitrate (NO_3^-), one of the most used additives in the food industry as well as fertilizer in the agricultural field [1], is also currently considered one of the major water contaminant. In fact, nitrate can alter into various harmful nitrogen-based compounds, like nitrite, nitric oxide, and N-nitroso compounds, which are reported to increase risks for human diseases such as cancer, Parkinson, gastritis, and blue-baby syndromes [2], [3]. Because of nitrate toxicological influence on human health, the World Health Organization (WHO) and European Directives have set a maximum contaminant level (MCL) of nitrate in public drinking water of 50 mg per liter (ca. 0.8 mM) [4]. To monitor nitrate levels in water, spectrophotometry, chromatography, and polarography are typically used [5]. Even if very sensitive, all the above-mentioned analytical methods are expensive and time-consuming. Sensitive, low-cost, easy-to-use, and disposable sensors for fast and accurate on-site analysis of nitrate are therefore extremely needed. At this aim, electrochemical detection methods are extremely attractive to detect nitrate, as well as various food toxicants, because of their high sensitivity and quick response [6]. To detect nitrate without the use of specific enzymes, which complicate the sensor fabrication process, many reactive materials have been employed including copper (Cu), cadmium (Cd), and lead (Pb). Among them, Cu has proven to be one of the most effective metals to electro-reduce nitrate ions [7], [8]. In particular, Cu works as a good catalyst for nitrate reduction because of its high conductivity ($5.8 \cdot 10^7$ S/m) improving charge transfer, providing active sites for the adsorption of NO_3^- [9]. Cu, especially in the form of nanoclusters can be easily deposited on different types of electrodes like glassy carbon, using electrodeposition technique as shown by Bagheri et al. [10]. Nevertheless, to the best of our knowledge, the electrodeposition of Cu on flexible screen-printed electrodes for the realization of nitrate sensor has never been reported. We present a novel flexible amperometric sensor for nitrate detection using both Cu and single-walled carbon nanotubes (SWCNTs) modified screen-printed electrodes. Screen-printing technique was selected because it is a viable fabrication technique, enabling the development of flexible, disposable, and cheap electrochemical sensors [11]. Additionally, SWCNTs were also employed due to their large area to volume ratio that can provide a large electroactive surface and a better sensor response [12],[13].

Therefore, in this work we decorated Cu nanoclusters with SWCNTs to improve the sensitivity of a screen-printed flexible electrode for nitrate detection. The sensor was realized by first coating the screen-printed working electrode (WE) with a layer of spray deposited SWCNTs and then electrodepositing Cu. The electrochemical performance of the Cu/SWCNTs/Ag sensors was analyzed and compared with the same sensor in absence of SWCNTs (Cu/Ag), proving the capability of SWCNTs to improve the sensitivity and the performance of the sensor thanks to the increase of the sensor electroactive surface area. Moreover, the sensor was fully operational after 1000 mechanical bending cycles and its overall performance was better (LOD 0.281 nM) as compared with recent literature where bulky and rigid electrodes were used (LOD 0.159 mM [5], 26 µM [14] and 20 nM [10]).

II. Methods

A. Electrode fabrication

A standard three-electrode sensor layout (Fig. 1) was realized on a 125 µm-thick polyethylene terephthalate (PET) substrate via screen-printing with a semi-automatic screen-printing machine (Aurel automation S.P.A. C290, Italy) using Ag (LOCTITE 1010) inks for the working and counter (WE, CE) electrodes and silver chloride (AgCl, LOCTITE 1011) ink for the reference electrode (RE). Then, the electrodes were annealed at 120 ºC for 15 min and cleaned with isopropyl alcohol and double-distilled water for 5 min

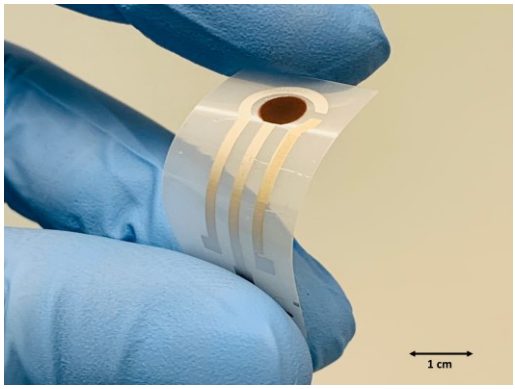

Fig. 1. Picture of the flexible screen-printed three-electrode nitrate sensor.

using bath sonication. To fabricate the Cu/SWCNTs/Ag sensors, SWCNT solution was prepared following [15]. Afterwards, 100 layers of SWCNTs were spray deposited on top of the WE through a stainless-steel shadow mask using an automated spray system (Nordson E4 EFD, UK) [16]. To deposit Cu on both Ag and SWCNT coated WE, electrodeposition was performed according to [5] through cyclic voltammetry (CV) using 0.1 M $CuSO_4.5H_2O/H_2SO_4$ (pH=2.0) at room temperature, in the potential range of –1.0 to 0 V with a scan rate of 0.1 Vs^{-1}. Later, the electrode was rinsed with double distilled water.

B. *Electrochemical and mechanical measurements*

The morphology of the Cu/SWCNTs/Ag electrodes was analyzed by scanning electron microscopy (SEM) (Quanta600f, FEI). All the electrochemical experiments were performed using a potentiostat (VersaSTAT 4 electrochemical workstation, Princeton Applied Research, USA) at room temperature. To understand the mechanism of electrode reaction and calculate the active surface area, peak current for nitrate reduction was investigated at different scan rates, from 25 to 500 mVs^{-1}, using CV at 3.0 mM $NaNO_3$ in 0.1 M KCl electrolyte solution in the potential range from -0.1 V to – 1.4 V. Linear sweep voltammetry (LSV) was applied to characterize the electrochemical behavior of nitrate on both Cu/SWCNTs/Ag and Cu/Ag sensors in the potential range of -0.1 to -1.4 V and for 0.01 V s^{-1} scan rate on different concentrations of NO_3^- (0.1 mM to 6.0 mM). To investigate the mechanical stability of the sensor, a mechanical bending test was conducted with a custom- made setup leading to a tensile bending of each sensor to a radius of 5 mm up to 1000 cycles.

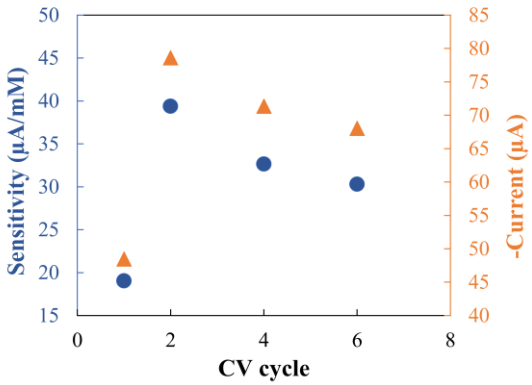

Fig. 2. Sensitivity and reduction peak current of nitrate sensor with silver (Ag) electrode coated with copper (Cu) nanoclusters and single-walled carbon nanotubes (SWCNTs) prepared through different cyclic voltammetry cycles of Cu deposition (for 1.6 mM nitrate).

III. Results and Discussion

A. *Electrochemical characterization*

To optimize the electrodeposition, 4 different numbers of CV cycles (1, 2, 4 and 6) were performed on top of SWCNT coated WE, examining each electrode with 4 different concentrations of nitrate (0, 0.1, 0.8, and 1.6 mM). As shown in Fig. 2, 2 CV cycles resulted in the highest sensitivity and peak current of nitrate reduction. Based on this result, 2 CV cycles were used for realizing both Cu/SWCNTs/Ag and Cu/Ag sensors.

B. *Surface characterization*

Fig. 3 shows the SEM micrograph of the electrodeposited Cu nanoclusters on the screen-printed Ag WE. From this image, it is noticeable that each SWCNT is covered by globular-shaped Cu nanoclusters, allowing the increment of the electroactive area. The measured diameter of a single Cu cluster is approximately within 200 to 500 nm range as reported in [17] and [18].

C. *Electrochemical calculation of the active surface area of the electrodes*

To evaluate the nature of the electrochemical reaction on both Cu/SWCNTs/Ag and Cu/Ag electrodes, the effect of the scan rate (v) on the reduction peak current was investigated. By plotting the peak current versus the square root of v (Fig. 4), a linear correlation (R^2) was established which showed that a diffusion-controlled process is occurring [19]. Moreover, the electrochemically effective surface areas of both Cu/SWCNTs/Ag and Cu/Ag electrodes have been calculated using the Randles-Sevcik equation [20]:

$$i_p = -2.99 \times 10^5 \, n \, \alpha^{1/2} \, A \, D_o^{1/2} \, v^{1/2} \, C \qquad (1)$$

where i_p is the peak current (A), n is the number of electron transfer (here it is 2 for NO_3^-), α is the cathodic electron transfer coefficient, A is the active surface area (cm^2), D_o is the diffusion coefficient (2.0×10^{-6} $cm^2 \cdot s^{-1}$ for NO_3^-), v is the scan rate (Vs^{-1}) and C is the nitrate concentration ($molcm^{-3}$).

The effective surface areas were found 0.042 cm^2 and 0.082 cm^2 for Cu/Ag and Cu/SWCNTs/Ag sensors respectively, showing thus that the presence of SWCNTs leads to an increase of the effective surface of 95.5%.

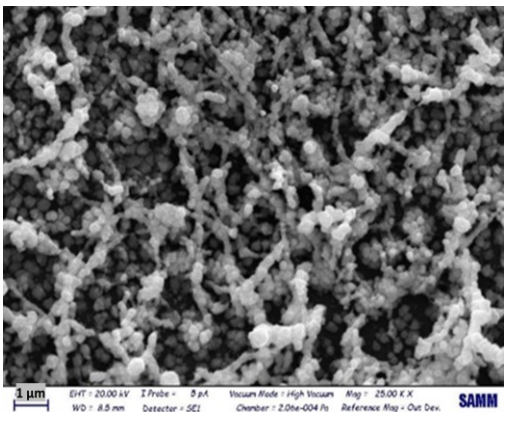

Fig. 3. Scanning electron microscopy (SEM) micrograph of Cu nanoclusters on top of Ag electrode coated with SWCNTs.

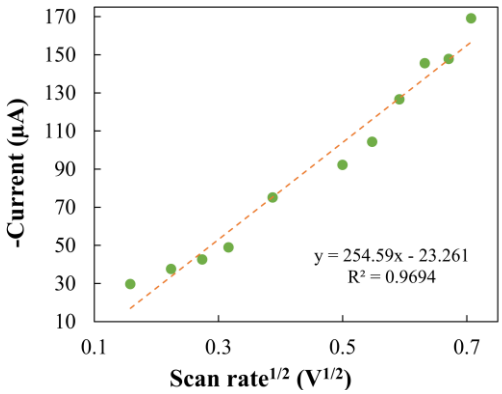

Fig. 4. Linear relationship of peak current versus square root of scan rate of nitrate sensor with Ag electrode coated with Cu and SWCNTs.

D. Sensor performance for nitrate detection

The analytical performance of the sensor to different concentrations (0, 0.1, 0.4, 0.8, 1.6, 3.0, 4.5, and 6.0 mM) of NO_3^- was determined by LSV, recorded at optimized experimental parameters for both Cu/SWCNTs/Ag and Cu/Ag electrodes. Fig. 5 shows the calibration curve for both sensors, plotted based on the nitrate reduction peak current which appeared at a potential of -0.85 V. The calibration curve shows a linear detection range from 0.1 mM to 6.0 mM for both electrodes, with good repeatability and reproducibility (SD ranges from 0.93 to 5.14 µA). As expected, the presence of SWCNTs enhances the sensor response, indeed the Cu/SWCNTs/Ag sensor sensitivity (18.19 µA/mM) was approximately 1.5 times higher than Cu/Ag sensor (12.19 µA/mM). Moreover, the R^2 increased from 98.63% to 99.75%. The limit of detection (LOD) was calculated from the following formula:

$$LOD = (3.3.\ STDEV\ I_o) / m \quad (2)$$

where I_o is the generated peak current of blank (0 mM) concentration of $NaNO_3$ and m is the slope of the linear response curve.

The calculated LOD was 0.381 nM and 0.218 nM for Cu/Ag and Cu/SWCNTs/Ag sensor respectively, which indicates that SWCNTs increase the electron transfer kinetics by improving the electroactive surface area.

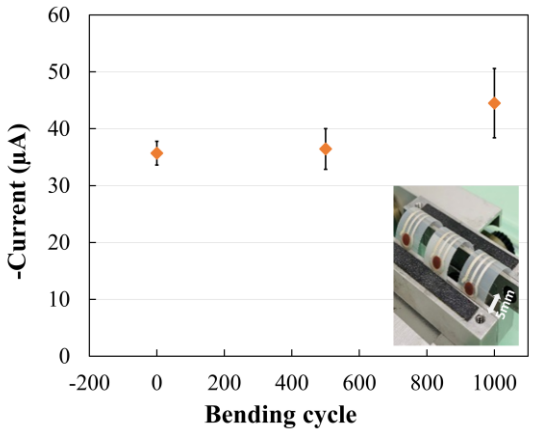

Fig. 6. Automated mechanical bendability test for screen-printed nitrate sensors (Inset: sensor while bent to a tensile radius of 5 mm).

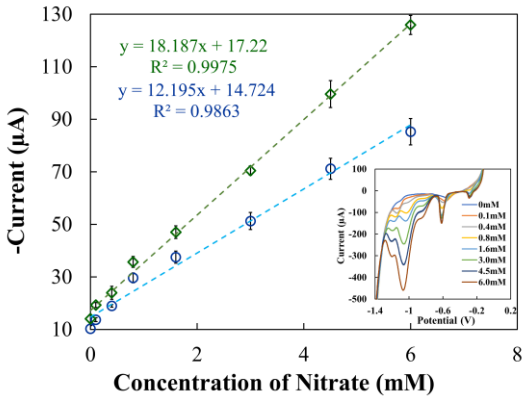

Fig. 5. Calibration curve of Cu/SWCNT/Ag and Cu/Ag sensor for nitrate detection. Error bars shown as a triple of the standard deviation (n = 3). Inset: LSV curve of Cu/SWCNT/Ag sensor at different nitrate concentrations.

E. Mechanical stability test

The mechanical stability of the Cu/SWCNTs/Ag sensor was examined by performing a bending test. The sensor was bent down to a radius of 5 mm for 500 and 1000 bending cycles and the reduction peak current after each cycle number was measured. As shown in Fig. 6, the current generation was well maintained after such repetitive bending cycles, proving the stability of the sensors to mechanical deformation. Nevertheless, the SD increased from ±2.07 µA to ±6.07 µA after 1000 bending, suggesting the possible formation of some permanent nano-cracks in the electrode.

IV. Conclusion

This study provides a flexible low-cost and easy-to-fabricate Cu/SWCNT modified screen-printed sensor for nitrate detection. While comparing the Cu/SWCNTs/Ag sensor with the Cu/Ag sensor, we demonstrated the possibility to improve the analytical behavior of the sensor using SWCNTs, which allow to increase the electron transfer kinetics and expand the electroactive surface area, up to 95.5%. Indeed, the Cu/SWCNTs/Ag sensor showed an enhanced sensitivity (1.5 times higher) and lower LOD compared to Cu/Ag sensor in the same testing conditions. In the future, the sensor stability versus time and selectivity will be addressed and the sensor will be tested with real water sample and the result will be validated by a reliable analytical technique like high-performance liquid chromatography (HPLC).

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