Electronic Supporting Information

Flexible screen-printed electrochemical sensor functionalized with electrodeposited copper for nitrate detection in water

AKM Sarwar Inam,[†,‡] Martina Aurora Costa Angeli,[†] Bajramshahe Shkodra,[†] Ali Douaki,[†] Enrico Avancini,[†] Luca Magagnin,[¶] Luisa Petti,[†,*] Paolo Lugli[†]

[†]Faculty of Science and Technology, Free University of Bozen-Bolzano, Bolzano, Italy
[‡]Department of Nutrition and Food Engineering, Daffodil International University, Dhaka, Bangladesh
[¶]Department of Chemistry Materials and Chemical Engineering "Giulio Natta" Politecnico di Milano, Milano, Italy

E-mail: *luisa.petti@unibz.it

1. Optimization of CV cycle

To optimize the number of CV cycle for Cu electrodeposition process, 6 different numbers of CV cycles (2, 5, 7, 10, 15, and 20) were performed on similar type screen-printed silver electrodes (WEs). After the electrodeposition, each electrode, characterized by different CV cycles of Cu electro-deposition, was examined with 4 different nitrate concentrations (0, 0.1, 0.8, and 1.6 mM). The reduction peak current versus nitrate concentration is plotted in Figure S1, where 10 CV cycles showed the highest sensitivity.
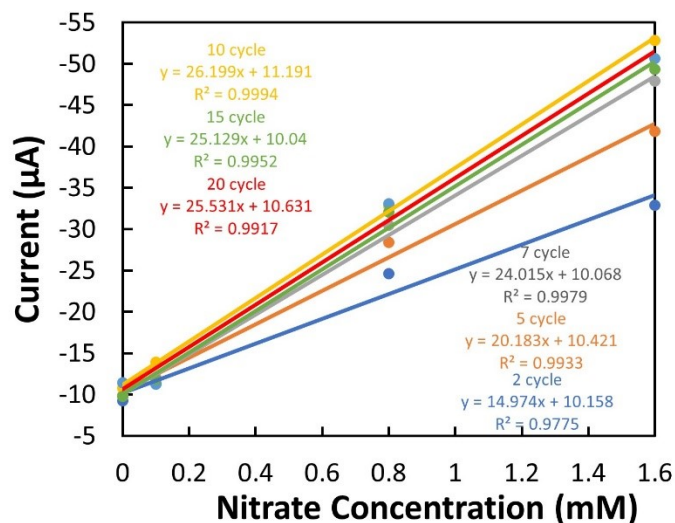

Figure S1: Optimization of cycle number of cyclic voltammetry (CV) based on cathodic current response of nitrate reduction. 6 different numbers of CV cycles (2, 5, 7, 10, 15, and 20) were performed on top of working electrode (WE). After the electro-deposition, each electrode was examined with 4 different nitrate concentrations (0, 0.1, 0.8 and 1.6 mM)

2. Morphological characterization of Cu deposition

Figure S2A shows the bare Ag WE characterized by a flakes like structure typical of screen-printing process. After electrodepositing Cu with 5 cycles of CV (Figure S2B), Cu did not uniformly cover the Ag flakes that were clearly visible. Instead, using 10 cycles of CV, Cu was uniformly distributed all over the Ag electrode, as shown in Figure S2C. On the other hand, from 15 CV cycles the surface showed an increase of Cu but only clustered in the area at higher Cu concentration (Figure S2D)
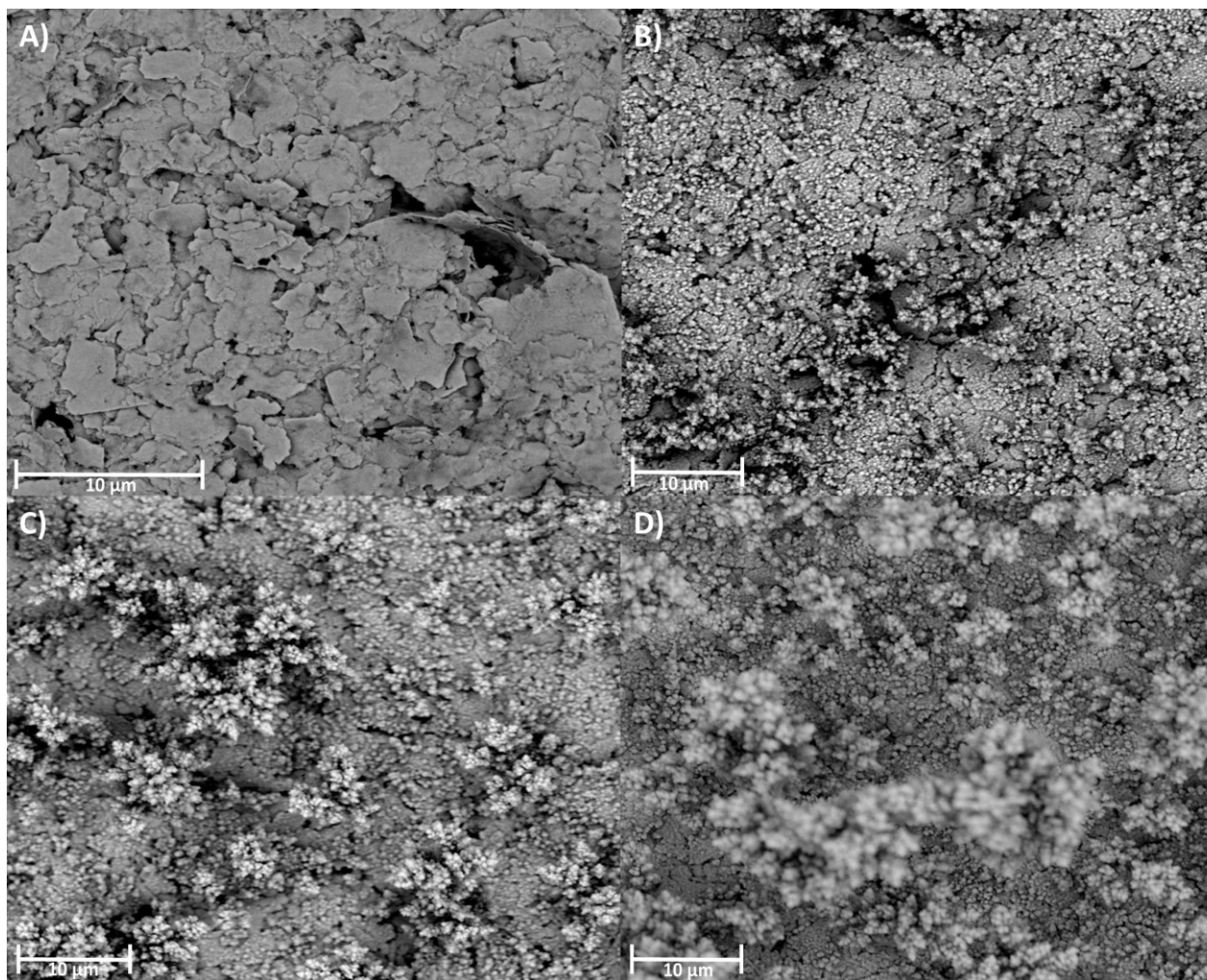

Figure S2: SEM images of screen-printed Ag WE modified with different numbers of CV of Cu electrodeposition : A) Bare Ag screen printed WE. B) 5 CV cycles of Cu electrodeposited on Ag WE. C) 10 CV cycles of Cu electrodeposited on Ag WE. D) 15 CV cycles of Cu electrodeposited on Ag WE.

EDS analysis is presented in Figure S3 to show the composition of the surface of the working electrode. The normalized mass concentration in Figure S3 allows observing that the surface of the electrode contains 80% of Cu, 15% of Ag, 4% of C, and 0.5% of O as expected. The value proves that most of the surface area of the screen-printed Ag electrode was covered of electrodeposited Cu.
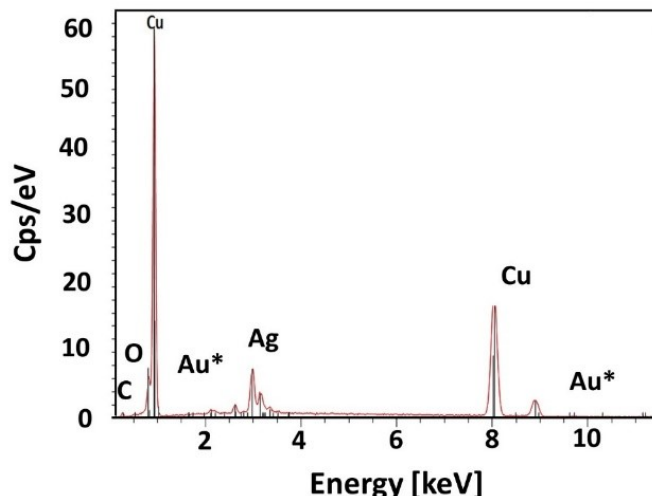

Figure S3: EDS pattern showing the normalized mass concentration in percentage

3. Half-peak potential of electrode

The potential at which the nitrate reduction occurs shifted negatively with the increment of scan rate as shown in Figure S4A. This characteristic behavior is associated with a diffusion-controlled irreversible electron transfer process.[1] To investigate the kinetics of an electrode, the half-peak potential $E_{p/2}$ is often examined.[2] The magnitude of $\Delta E_{p/2}$ (= $E_p - E_{p/2}$) was calculated and plotted against the scan rate as shown in Figure S4B.
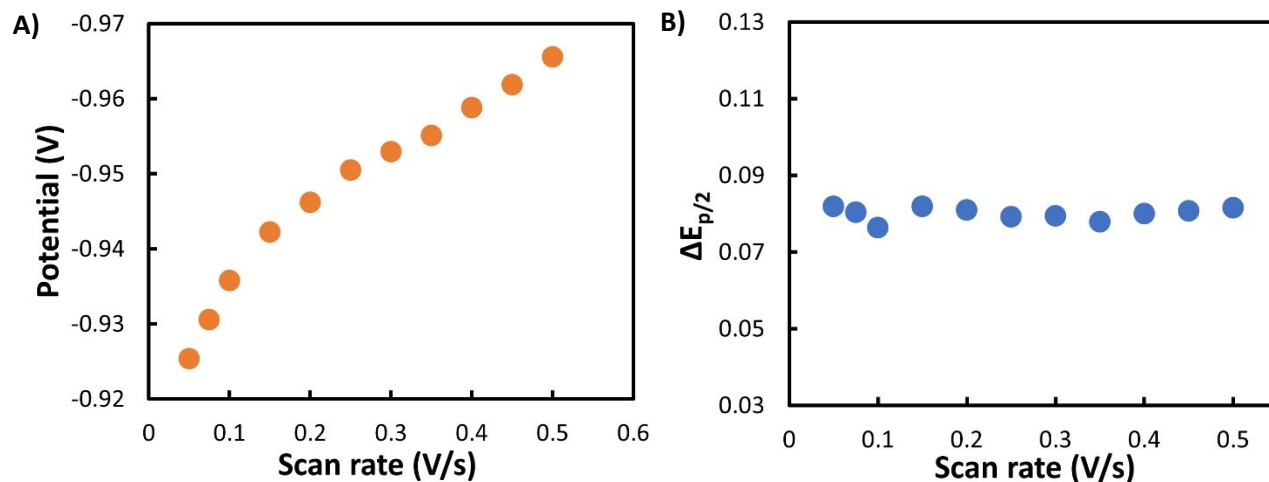

Figure S4: A) Dependency of the NO_3^- reduction peak potential at different scan rates of the Ag/Cu electrode. B) Scan rate dependency of $\Delta E_{p/2}$ for the nitrate reduction

4. Nitrate detection using Cu curve

The amplitude of the reduction peak of Cu (II) increased linearly with the increasing nitrate concentration. This observation can be explained by the catalytic effect of the copper. Filimonov et al.[3] showed that cuprous ion exhibits the catalytic effect with nitrogen-containing any compound which is electrochemically active and thus, Cu(II) peak (Figure S5) can also be used to detect the nitrate.
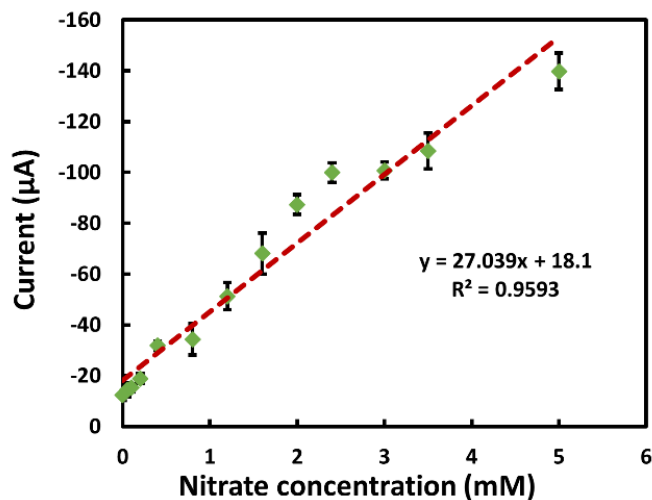

Figure S5: Linear relationship between reduction peak current of Cu(II) with different NO_3^- concentration. Each point represents the average peak current performed by 3 sensors, where the standard deviation with error bars is shown.

5. Interference test

The influence of Cl^- was investigated as Cl^- is considered as one of the most potential interfering agents[4,5] and also the main component of the electrolyte solution employed. Since 0.1 M KCl was used as the electrolyte in this work, other two different concentrations of KCl (0.5 M and 1 M) have been prepared and mixed with 0.8 mM of $NaNO_3$ to investigate the possible interference on the cathodic reduction peak, as shown in Figure S6A. The selectivity of the Ag/Cu sensor was investigated by evaluating the change of the reduction peak of nitrate (at -0.85 V) in the presence of 0.8 mM of different possible interfering ions (NO_2^-, HCO_3^-, SO_4^{2-}, Fe^{2+}, Fe^{3+}, CH_3COO^-, Mn^{2+}, Na^+ and Cu^{2+}. As shown in Figure S6B, the amplitudes of the current peak at -0.85V for all these interferents were similar to the value of the blank solution (0 mM $NaNO_3$ in 0.1 M KCl).
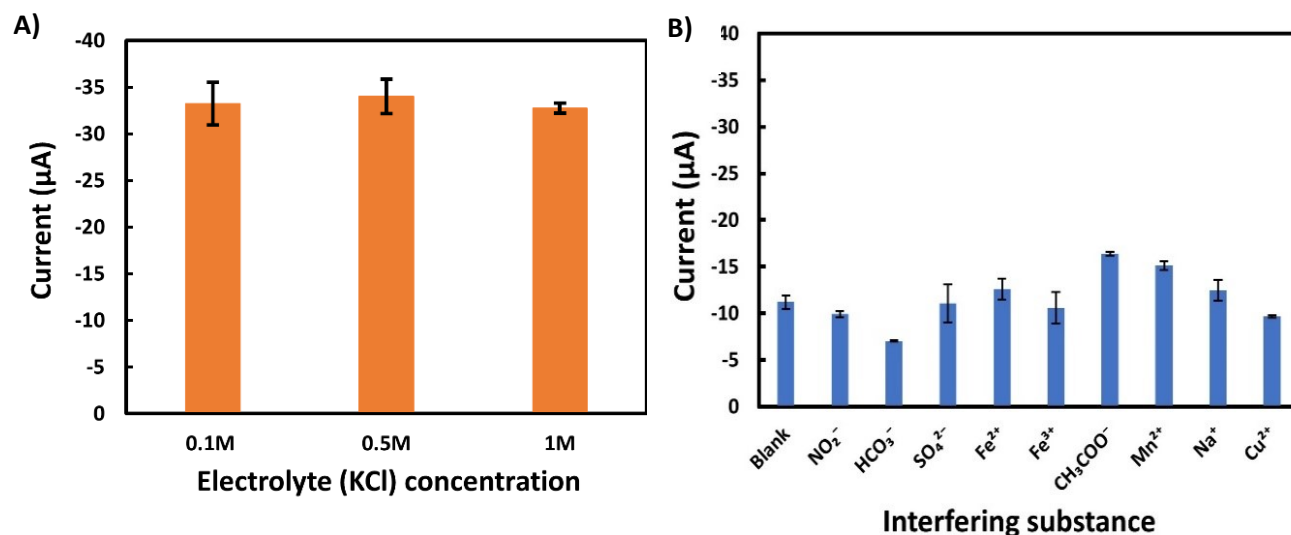
Figure S6: A) Interference of nitrate reduction peak current for different concentrations of KCl. B) Interference of reduction peak current at -0.85 V with the presence of NO_2^-, HCO_3^-, SO_4^{2-}, Fe^{2+}, Fe^{3+}, CH_3COO^-, Mn^{2+}, Na^+ and Cu^{2+}.

6. Repeatability test

For the repeatability test, same sensor was tested 10 consecutive times and the reduction current peak at 0.8 mM of NO_3^- was compared with the first measurement to calculate the relative standard deviation (RSD), as shown in Figure S7. Each time after examining the sensor with nitrate, the sensor was rinsed with DI water and dried with compressed air and kept ready for the next test. The sensor has stable behavior only up to the second measurement.
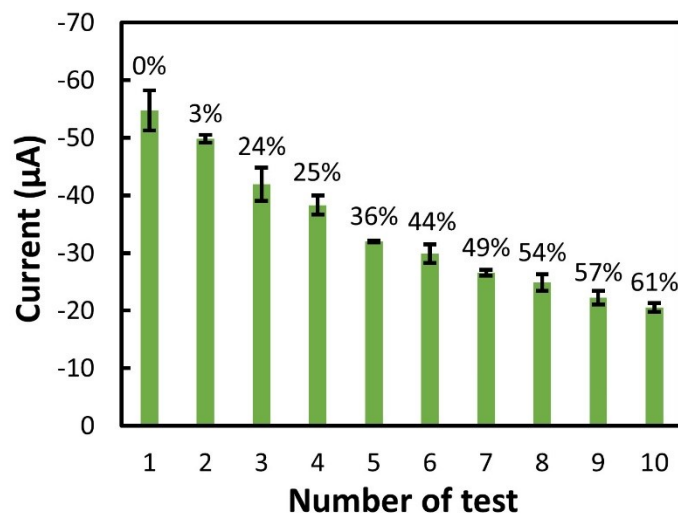

Figure S7: Repeatability test for Cu/Ag sensor. The reduction peak current of the NO_3^- was taken from same sample repeating 10 times measurement. The percentage is the value of degradation of the electrode compared to the first one.

References:

(1) Polatides, C.; Kyriacou, G. Electrochemicalreduction of nitrate ion on various cathodes –reaction kinetics on bronze cathode. J. Appl. Electrochem. **2005**, 421–427.

(2) Bontempelli, G.; Dossi, N.; Toniolo, R.Chemistry, Molecular Sciences and Chem-ical Engineering/Linear Sweep and Cyclic;Elsevier Inc., **2016**, pp 1–10.

(3) Filimonov, E. V.; Shcherbakov, A. I. Catalytic Effect of Copper Ions on Nitrate Reduction. *Prot. Met.* **2004**, *40* (3), 280–285.

(4) Dima, G. E.; De Vooys, A. C.; Koper, M. T.Electrocatalytic reduction of nitrate at lowconcentration on coinage and transition-metal electrodes in acid solutions.J. Elec-troanal. Chem. **2003**, 554-555, 15–23.

(5) Da Silva, I. S.;De Araujo, W. R.;Paixão, T. R.; Angnes, L. Direct nitratesensing in water using an array of copper-microelectrodes from flat flexible cables. Sens. Actuators, B. **2013**, 188, 94–98.