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An inverse-designed electrochemical platform for analytical applications

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ABSTRACT

Screen-printed electrodes are the most recent generation of low-cost, mass-produced, sensitive and portable devices for the measurement of analytes of interest. The responses of these platforms, in terms of current intensity and reproducibility, are strongly influenced by factors such as printing procedures, type of ink, substrates, etc. In this paper, an improved inverse-designed screen-printed electrode (IDSPE) is proposed. The electrochemical performance is compared with that obtained using classical screen printed electrodes (SEPs), showing enhanced sensitivity and signal-to-noise ratio (background current minimization 32 ± 3nA and 0.64 ± 0.01nA, for SPE and IDSPE, respectively). A full comparison between inverse and classical screen-printed electrodes is carried out using various electroactive species (potassium ferricyanide, ascorbic acid, hexaammineruthenium(III) chloride and NADH) and two different electrochemical techniques (cyclic and square-wave voltammetry). In tests conducted with potassium ferricyanide the sensitivity of the IDSPE shows a nearly four-fold improvement, and a limit of detection three times better than the values obtained employing the classical SPE. The reproducibility (RSD%) in tests conducted with ascorbic acid is 6% and 12% for IDSPE and SPE, respectively. Moreover, surface modification of both screen-printed electrodes (SPE and IDSPE) with biochar obtained from recycled brewers waste (Bio-SPEs and Bio-IDSPEs), further improves their electrochemical performance, in terms, for example, of the heterogeneous electron transfer constant (0.0024 and 0.0018 for Bio-SPE and Bio-IDSPE, respectively).

1. Introduction

Screen-printing technology is now a well-established technique for the mass production of electrochemical sensors with good sensitivity and selectivity but limited repeatability. Since the 1990s, this technique has offered high-volume production of inexpensive, dependable sensors, which has paved the way for on-site monitoring and analysis of various chemicals using portable instruments in clinical, environmental and food-testing applications. Indeed, disposable and cost-effective biosensors based on screen-printed electrodes (SPEs) modified with selective bioreceptors have led to new opportunities in the evaluation and quantification of polluting biomolecules, viruses, bacteria, microorganisms and enzymes [1–3]. SPEs typically include working, counter and reference electrodes (WE, CE and RE, respectively) printed on various types of substrates (plastics, paper or ceramic), which allow these platforms to be modified according to the area of application, and the sensitivity and accuracy required [4]. Silver ink is printed as a conducting track and the RE, CE and WE are printed on the track. The CE is normally graphite, and WEs are usually printed using graphite, gold, or platinum-based inks [5,6]. The sensitivity and reliability of graphite SPE platforms are usually considered acceptable for most purposes, but for high-precision measurements they can lead to erroneous or

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unreliable outputs at times [7]. In recent years, bare graphite SPEs have often been modified with nanomaterials or nanoparticles to obtain higher sensitivity in the micro- or nano-molar concentration ranges [8–11]. Furthermore, many researchers have been working on recycling procedures to recover plant biomass [12], producing biochar, which is extracted by a thermal process [13]. Biochar, whose morphological and electrochemical characteristics have already been described by Cancelliere at al. [14], has a carbon microstructure with good electrochemical performance, providing excellent electron transfer kinetics, high sensitivity and repeatability and wide potential applicability thanks to its inert inner structure and its highly functionalizable surface [14,15]. These structural characteristics are very similar to those of nanomaterials widely used in electrochemistry (i.e., graphene, nanotubes, and nanofibers) [16], making biochar an alternative for the production of SPEs based on renewable and biocompatible resources. There is, in fact, growing interest in the use of eco-friendly materials for electronics, giving rise to an innovative generation of high-performance green modifiers [12,17]. Despite these advances, it is still desirable to develop new electrochemical platforms with improved repeatability and sensitivity.

In this overall scenario, we propose an inverse-designed screen-printed electrode (IDSPE) by reversing the extent of the RE and CE, producing an increase in the signal/noise ratio and reproducibility, compared to the classical SPE. Indeed, this paper shows that the different electrode layout represents a technological advance of the SPE. In addition to this new configuration, SPEs and IDSPEs have been compared with biochar-modified electrodes (Bio-SPE and Bio-IDSPE, respectively). The electrochemical characterization of these modified platforms highlighted a significant reduction in overall measurement variability, producing outputs that are more sensitive. The analytical performance of IDSPEs compared with normal SPEs, using different electroactive substrates, demonstrates the greater sensitivity and reproducibility of the IDSPEs thanks to a more stable potential difference between the WE and RE.

2. Experimental

2.1. Materials

All chemicals from commercial sources were of analytical grade. Biochar, supplied by CREA Research Center (Rome, Italy), was obtained via a pyrolytic micro-gasification process (T = 400° C) in an Elsa D17 micro pyrolytic reactor (Bluecomb Ltd., Udine, Italy) [14]. Ethanol, hexaammineruthenium (III) chloride, L-ascorbic acid, NADH and potassium chloride were purchased from Sigma-Aldrich (Steinheim, Germany). Potassium ferricyanide was purchased from Fluka Chemie, Sigma-Aldrich (Buchs, Switzerland). The buffer solution was 0.05 M phosphate buffer saline (PBS) + 0.1 M KCl, pH = 7.4.

2.2. Electrodes

All the electrodes were produced in-house with a 245 DEK high-performance multi-purpose precision screen-printing machine (Weymouth, UK). Graphite-based ink (Elettrodag 421) from Acheson (Milan, Italy) was used to print the working and counter electrodes. The electrode scaffold was a folding polyester film (Autostat HT5) obtained from Autotype Italia (Milan, Italy). The electrodes were produced in foils of 48 electrodes (SPEs). The diameter of the WE was 0.3 cm, resulting in an apparent geometric area of 0.07 cm^2. Silver ink was used to print the reference electrode (Acheson Elettrodag 4038 SS). The application of an insulating print (Argon Carbonflex 25.101S) defined the actual surface area of the WE.

2.3. Apparatus

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed using an Autolab electrochemical system equipped with PGSTAT-15 and GPES software (Eco Chemie, Utrecht, The Netherlands). Biochar dispersions were obtained using a Hielscher UP200St-Ultrasonic Transducer (GmbH, Germany).

2.4. Procedures

2.4.1. Preparation of biochar-modified SPEs

The biochar-modified SPEs were prepared as follows. Prior to the modification step, the SPEs were pre-treated in a 0.05 M phosphate buffer + 0.1 M KCl, pH 7.4, by applying a constant anodic potential of 1.7 V for 180 s and rinsed with distilled water to remove salt residues that could have interfered with the electrochemical measurements. A biochar dispersion (1 mg mL^{-1}) was prepared at room temperature (RT) by dissolving the carbonaceous material in a 2:1 (v v^{-1}) ethanol − water mixture and applying the ultrasonic transducer (amplitude and frequency, 200 W and 26 kHz, respectively) for 30 min. 6 μL of the resulting dispersion was deposited on the WE via a drop-casting procedure [9,14,16]. The electrodes were then allowed to dry for one hour at RT.

2.4.2. Calculation of analytical parameters

The limit of detection (LOD) is estimated from the analysis of ten samples (blanks) in which the analyte is not present using the formula:

$$\mathrm{LOD} = \frac{3 \cdot \mathrm{SD}_{\mathrm{blank}}}{S} \tag{1}$$

were SD $_{\mathrm{blank}}$ is the blank's standard deviation (over ten samples) and S is the sensitivity of the analytical method (the slope of calibration line).

The electronic transfer process is studied using the heterogeneous rate constants (k^0) for the redox process: $[\mathrm{Fe(CN)_6}]^{3-} + 1\mathrm{e}^- \rightleftarrows [\mathrm{Fe(CN)_6}]^{4-}$. The k^0 was calculated using the following equation [18]:

$$k^0 = \varphi \sqrt{\frac{D_O \pi \nu n F}{RT}\left(\frac{D_R}{D_O}\right)^{\alpha}} \tag{2}$$

where D_O and D_R are the diffusion coefficients for ferricyanide (D_O) and ferrocyanide (D_R), ν is the scan rate (V s^{-1}), n is the number of electrons involved in the process, T is the temperature (K), F is the Faraday constant (mol^{-1}), R is the universal gas constant (J $K^{-1}mol^{-1}$) and α the dimensional transfer coefficient [19]. The parameter φ is obtained using the Nicholson method [18,20]:

$$\varphi = \frac{(-0.6288 + 0.0021 \cdot \Delta E)}{(1 - 0.0170 \cdot \Delta E)} \tag{3}$$

where ΔE is the potential difference between anodic and cathodic peaks.

The Randles-Sevcik equation (equation (4)) was used to investigate the electrochemical behavior of the different platforms:

$$I_p = (0.4463) nFAC \sqrt{\frac{nF\nu D_O}{RT}} \tag{4}$$

where I_p is the current peak, F is the Faraday constant (mol^{-1}), R is the universal gas constant (J $K^{-1}mol^{-1}$), n the number of electrons exchanged, A the area of the electrode surface (cm^2), C the analyte concentration (mol cm^{-3}), D_O the diffusion coefficient (cm^2 s^{-1}), and ν the scan rate (mV s^{-1}).

3. Results and discussion

3.1. Design characteristics typical of IDSPEs

There are many electrochemical systems where the design principles are generally the same [21]. The configuration normally features a three-electrode system (WE, CE and RE) (Fig. 1) [22,23]. In this configuration, the role of the CE is to generate the current needed to balance the current observed at the WE, but in doing so the counter is

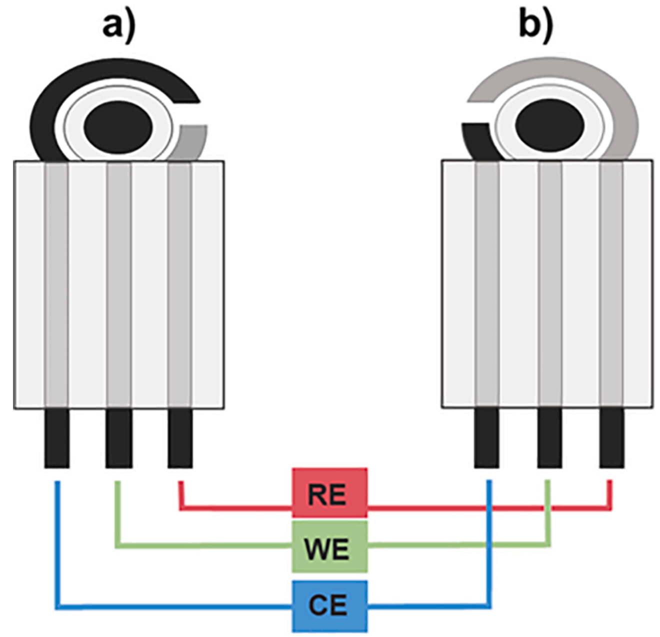

Fig. 1. Schematic representations of (a) conventional SPE and (b) IDSPE.

not be able to measure the exact potential at which the chemical cell effectively operates. This role is taken by the RE, which is left floating to balance the actual potential of the solution in that position. The RE potential is compared against any desired operating voltage level and the differential signal or "error" is used to drive the CE until the measured RE potential is fully balanced in the solution to the desired value, minimizing the error. The critical role of the RE and its ability to report the true cell potential is extremely important for the reproducibility of the measurements [2]. A symmetrical geometry for the RE with respect to the WE is generally preferred. The RE configuration of the inverse-designed electrode (shown in Fig. 1b) offers better cylindrical symmetry around the central WE and guarantees a uniform potential difference around almost all of the WE with respect to the SPE. Moreover, the wider area of the Ag deposit comprising the RE in the IDSPE significantly extends the operational lifetime of the cell, the effect of the oxidation and deterioration of the surface being better tolerated by the larger area. the modification which gave rise to this inverse-designed electrochemical platform is simply achieved by inverting the counter and reference electrodes. This can be done by modifying the printing sequence but using the same inks and frames. Using this alternative preparation method, the electrodes can be produced in roughly the same time as classical electrodes, keeping the production cost approximately equivalent.

3.2. Comparison of the electrochemical performances of IDSPEs and Bio-IDSPEs with SPEs

The use of IDSPEs minimizes the background current, producing a more dependable electrochemical device. The current output was quantified using ten different electrodes to measure 100 mM KCl solution using amperometry (1.7 V, 150 s) as the analytical technique [24]. Specifically, the following current results were obtained: 0.64 ± 0.01nA and 32 ± 3nA for IDSPE and classical SPEs, respectively, where the standard deviation [25] is used as the index of signal/noise ratio. CV and SWV techniques were used for electrochemical characterization of the classical SPEs, IDSPEs, Bio-SPEs and Bio-IDSPEs employing $[Fe(CN)_6]^{4-/3-}$, ascorbic acid ($C_6H_8O_6$), hexaammineruthenium(III) chloride ($Ru(NH_3)_6Cl_3$) and NADH ($C_{21}H_{27}N_7O_{14}P_2$) as electroactive probes. The results for all the different platforms (SPEs, IDSPEs, Bio-SPE and Bio-IDSPEs) in terms of anodic and cathodic peaks (ΔE), limit of detection (LOD), sensitivity and reproducibility are reported in Table 1. Fig. 2 shows the voltammograms obtained using $Ru(NH_3)_6Cl_3$ as example.

Additionally, only for potassium ferricyanide, the voltammetric peak heights (I_p) related to the SPEs and IDSPEs were monitored as a function of the scan rate (Fig. 3a and 3b) and afterwards plotted against the square root of the scan rate ($\nu^{0.5}$), following the Randles-Sevcik equation (Eq. (4)). This experiment was carried out for the different platforms, and the following slopes ($(\mu A/(mVs^{-1})^{0.5})$) were obtained using potassium ferricyanide as electroactive probe: 1.28 ($r^2 = 0.995$) and 1.46 ($r^2 = 0.997$), for the SPEs and IDSPEs, respectively. The voltammograms acquired at 50 mV s^{-1} are characterized by a variable estimate of ΔE. The SPE and IDSPE showed values of ΔEs equal to 554 and 430 mV, respectively, which represents a significant improvement towards ideal electrochemical behaviour for the IDSPE.

Starting from these promising results, two drop-cast platforms were prepared: Bio-SPE and Bio-IDSPE, and these were electrochemically studied using the same electroactive species as described above. The corresponding voltammograms are reported in Fig. 2(d), (e) and (f); the electrochemical parameters of interest are reported in Table 1.

Bio-SPE and Bio-IDSPE, analysed using potassium ferricyanide as electrochemical probe, showed ΔE equal to 270 and 205 mV, respectively, much lower than the values for the classical SPE and IDSPE, which represents an important advance toward ideal electrochemical behaviour. The voltammetric peak heights (I_p) for the Bio-SPEs and Bio-IDSPEs were monitored as a function of the scan rate (Fig. 3c and 3d) and plotted against the square root of the scan rate ($\nu^{0.5}$). The slopes ($(\mu A/(mV\ s^{-1})^{0.5})$) obtained were 1.38 ($r^2 = 0.998$) and 1.58 ($r^2 = 0.998$), corresponding to Bio-SPE and Bio-IDSPE, respectively (a two-fold increase in sensitivity compared with the unmodified SPEs). The bio-modified electrodes led to a large improvement in electron transfer for this particular redox probe compared to bare and conventional SPEs. Specifically, the value of the electron transfer rate constant (k_0) is equal to 0.0024 and 0.0018 for Bio-SPE and Bio-IDSPE, respectively [14]. Finally, the modification with biochar strongly enhances reproducibility

Table 1

CVs analysis: cathodic and anodic potential difference, sensitivity, inter-electrode reproducibility and LOD (SWV), calculated for potassium ferricyanide ($[Fe(CN)_6]^{4-/3-}$), hexaammineruthenium(III) chloride ($Ru(NH_3)_6Cl_3$), ascorbic acid ($C_6H_8O_6$), and NADH ($C_{21}H_{27}N_7O_{14}P_2$) for SPE, IDSPE, Bio-SPE and Bio-IDSPE.

		SPE	IDSPE	Bio-SPE	Bio-IDSPE
Potassium ferricyanide	ΔE (mV)	554	430	270	205
	LOD (μM)	9	3	5	1
	Sensitivity (mA/M cm^2)	40	10.7	16.8	6.4
	Reproducibility (RSD%)*	9.6	7.4	4.8	4.4
Hexaammine-ruthenium chloride	ΔE (mV)	174	159	163	154
	LOD (μM)	16	9	13	0.5
	Sensitivity (mA/M cm^2)	6.1	1.8	4.3	1.1
	Reproducibility (RSD%)*	11.3	6.6	6.5	5.5
Ascorbic acid	E_{ox} (mV)	442	410	410	345
	LOD (μM)	3	3	1	0.2
	Sensitivity (mA/M cm^2)	12.9	11.4	3.5	1.2
	Reproducibility (RSD%)*	12.7	5.9	6.9	5.4
NADH	E_{ox} (mV)	560	480	430	410
	LOD (μM)	20	12	6	3
	Sensitivity (mA/M cm^2)	21.3	8.4	6.5	4.7
	Reproducibility (RSD%)*	11.3	7.2	5.8	4.7

*RSD% indicates relative standard deviation *100; E_{ox} due to the irreversible oxidation

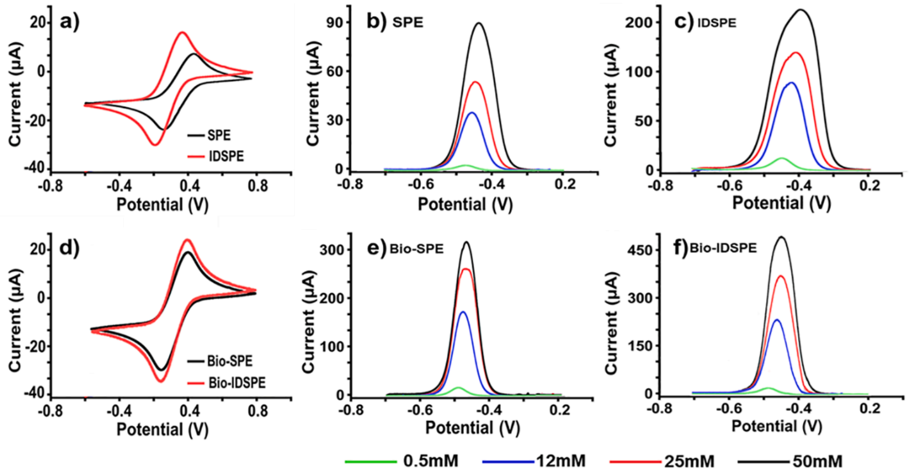

Fig. 2. Comparison of CV and SWV traces recorded using SPE, IDSPE, Bio-SPE and Bio-IDSPE. (a) and (d) show the CV traces of SPE, IDSPE and Bio-SPE, Bio-IDSPE, respectively (cast with 6 μL of 1 mg ml^{-1} biochar dispersion in a 0.05 M phosphate buffer + 0.1 M KCl, pH 7.4) in the presence of 25 mM hexaammineruthenium(III) chloride. All traces were recorded at a scan rate of 50 mV s^{-1}. Voltammogram traces (SWV) recorded using (b) SPE, (c) IDSPE, (e) Bio-SPE and (f) Bio-IDSPE (6 μL of a 1 mg mL^{-1} dispersion of biochar, in a 0.05 M phosphate buffer + 0.1 M KCl, pH 7.4) in the presence of hexaammineruthenium (III) chloride 0.5, 12, 25 and 50 mM; scan rate 50 mVs^{-1}.

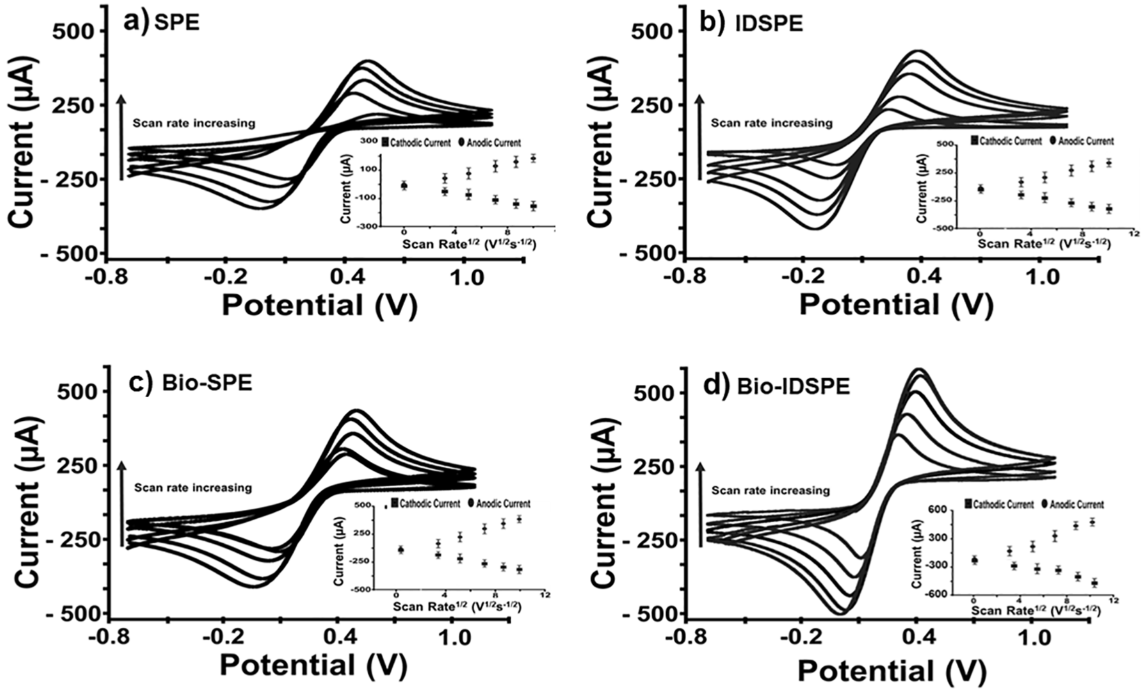

Fig. 3. CV traces recorded at different scan rates (100, 75, 50, 25 e 10 mV s^{-1}) with (a) classical SPE, (b) IDSPE, (c) Bio-SPE and (d) Bio-IDSPE in the presence of 50 mM ferricyanide solution in 0.05 M phosphate buffer + 0.1 M KCl, pH 7.4.

(RSD% values lower than for the unmodified platforms), sensitivity and LOD compared to the electrochemical platforms lacking this carbonaceous material.

4. Conclusions

This work focuses on the electrochemical characterization of inverse-designed SPEs (IDSPEs). Compared to classical SPEs, IDSPEs showed higher sensitivity (about a four-fold increase) and repeatability (RSD 3% lower than for classical SPEs), which we ascribe to the more stable reference potential application and to reduced overpotential and/or low background current produced by inverting the printing procedure. This trend has been observed for all the different electroactive compounds tested (potassium ferricyanide, ascorbic acid ($C_6H_8O_6$), hexaammineruthenium(III) chloride ($Ru(NH_3)_6Cl_3$) and NADH ($C_{21}H_{27}N_7O_{14}P_2$)), pointing to the higher dependability of this new generation of SPEs.

When SPEs and IDSPEs are modified with low-cost pyrolytic waste material (Bio-SPEs and Bio-IDSPEs), they showed even better electrochemical performances, including improved heterogeneous electron transfer constant, sensitivity, LOD and reproducibility values. Future work could focus on testing the proposed electrochemical platforms with clinical samples (i.e., blood, urine, serum, saliva) to look into the possible problem of fouling. In practice, undesirable compounds present in complex matrix samples tend to become attached to the reference electrode through various interactions, including hydrophobic, electrostatic and intermolecular forces, resulting in a dense layer that passively forms on the electrode with an alteration in the electrochemical response [26–28]. Finally, the study showed that the inverted printing approach is universally implementable and could open up new avenues in the manufacture of electrochemical biosensors with improved analytical performance while utilizing recycled material (biochar).

CRediT authorship contribution statement

Rocco Cancelliere: Validation, Formal analysis, Investigation, Writing - original draft. **Alessio Di Tinno:** Validation, Formal analysis, Investigation, Writing - review & editing. **Andrea Maria Di Lellis:** Conceptualization. **Yannick Tedeschi:** Conceptualization. **Stefano Bellucci:** Visualization. **Katya Carbone:** Resources, Visualization. **Emanuela Signori:** Writing - review & editing. **Giorgio Contini:** Conceptualization, Writing - review & editing. **Laura Micheli:** Investigation, Supervision, Project administration, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2020.106862.

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