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Simple and rapid fabrication of disposable carbon-based electrochemical cells using an electronic craft cutter for sensor and biosensor applications

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ABSTRACT

This work describes the construction of an all-plastic disposable carbon-based electrochemical cell (DCell) using a simple procedure based on the use of a home cutter printer for prototyping and laminating. The cutter printer and adhesive vinyl films were used to produce three electrodes in an electrochemical cell layout, and a laminating process was then used to define the geometric area and insulate the electrodes. The DCell showed excellent performance in several applications including the determination of toxic metals in water samples, the immobilization of DNA and the detection of *Salmonella*. An unmodified DCell was applied for Pb and Cd detection in the range of 100–300 ng mL^{-1} with a limit of detection of 50 and 39 ng mL^{-1} for Cd and Pb, respectively. DNA was successfully immobilized on a DCell and used for studies of interaction between bisphenol A and DNA. The square wave voltammetry of a DNA modified DCell presented a guanine oxidation current 2.5 times greater after exposure of the electrode to bisphenol A and no current variation for the adenine moiety indicating that bisphenol A showed a preference for DNA interaction sites. A magneto-immunoassay was developed using a DCell for *Salmonella* detection in milk samples. The system presented a linear range from 100 to 700 cells mL^{-1} with a limit of detection of 100 cells mL^{-1} and good recovery values between 93% and 101% in milk samples, with no interference from *Escherichia coli*. Using the proposed method, hundreds of DCells can be assembled in less than two hours, at a material cost of less than US $0.02 per cell. The all-plastic disposable electrochemical cell developed was successfully applied as an electrochemical sensor and biosensor. The feasibility of the developed all-plastic disposable electrochemical cell was demonstrated in applications as both sensor and biosensor.

1. Introduction

With the advent of disposable carbon-based electrodes, the development of sensors and biosensors has become much more accessible. These electrodes can be easily prepared, at low-cost and with good reproducibility, and they can be mass-produced [1]. The techniques normally used to fabricate disposable carbon-based electrodes are screen-printing and inkjet printing. The screen-printing technique involves using a squeegee to force a thixotropic conducting ink through a mesh screen that defines the geometry of the electrode. Different mesh screens are usually used to print different parts of the electrode, and each step requires a thermal treatment for curing and adhesion of the ink. An insulating ink is used to define the electrode geometry and insulate the conductive track [2–5]. In inkjet printing processes, the ink is transferred and patterned directly onto the substrate from a nozzle, in the same way as a home inkjet printer [6,7]. In this case, after printing the carbon electrode, the cartridge must be replaced in order to print the reference electrode or the insulation. This system has the advantage of being able to directly print different materials, such as gold nanoparticles [8], carbon nanotubes [9], graphene [10] and conducting polymers [11]. However, both techniques are costly and involve time-consuming operations. The usual screen-printing method requires costly machines and the design and fabrication of specific stencils, screens, and rollers; while inkjet-printing techniques requires modification of the physical properties of the ink in order to avoid printability problems. For these reasons, purchase of commercial disposable carbon-based electrodes is the usual preferred option instead of construction of the electrodes, despite their relatively high cost.

Recently, the use of electronic craft cutter printers to develop

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electrodes and flow systems devices has increased, due to the popularization of those printers. Cutting of adhesive vinyl films has been used to prepare inexpensive stencils for the construction of gold electrodes with highly reproducible areas from recordable compact discs [12] and screen-printed carbon electrodes using graphic papers [13] and cotton [14] as substrates. Flexible microfluidic devices have been constructed using craft printers based on double-sided pressure sensitive adhesive tape and laser printer transparency film [15] and by carving channels in a sheet of cardstock paper [16].

This work describes a simple procedure for the construction of all-plastic disposable electrochemical cells (DCell) using an inexpensive (less than US $300.00) home cutting printer and a laminating process. Using the printer, a stencil with the pattern of the electrodes could be easily produced in adhesive vinyl films. The stencil was attached to a polyester sheet and the electrodes were screen-printed. The stencil was used as mask or area delimiter for electrodes of different materials. A lamination pouch was used to define the geometric area and insulate the electrodes. Hundreds of DCells could be produced in less than 2 h, at a cost of less than US $0.02 per DCell. The concept was demonstrated using the DCells in different applications such as the determination of toxic metals in water samples, immobilization of double-stranded DNA and its interaction with bisphenol A, and in the electrochemical detection of *Salmonella* in milk samples.

2. Material and methods

2.1. Chemicals and reagents

Ruthenium hexamine(III) chloride, HPLC grade acetic acid and sodium acetate, calf thymus DNA, bisphenol A, bovine serum albumin, hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), trisodium citrate, 1-(3-(dimethylamino)-propyl-3-ethylcarbodiimide hydrochloride, N-hydroxysuccinimide, and NADH (CAS number 104809-32-7) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium phosphate monobasic (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4), potassium chloride (KCl), sodium chloride (NaCl), sodium hydroxide (NaOH), nitric acid (HNO_3, 65%), and Tween 20 were obtained from Merck (Darmstadt, Germany). Carboxyl functionalized magnetic beads (MBs) were obtained from Polysciences, Inc. (Prod. no. 86011-10, Warrington, PA, USA). Anti-*Salmonella* polyclonal primary antibody (pSAb) (Product no. 01-91-99), *Salmonella Typhimurium* (S) (Product no. 50-74-01), and *Escherichia coli* O157:H7 were obtained from KPL Inc. (Gaithersburg, Maryland, USA). Anti-*Salmonella* monoclonal second antibody (sSAb) (Product no. ab8273) was purchased from Abcam (Cambridge Science Park, Cambridge, UK). All chemicals used for the preparation of stock and standard solutions were analytical grade, unless otherwise stated. Working solutions were prepared with ultrapure water obtained from a Milli-Q system (Millipore, Bedford, USA).

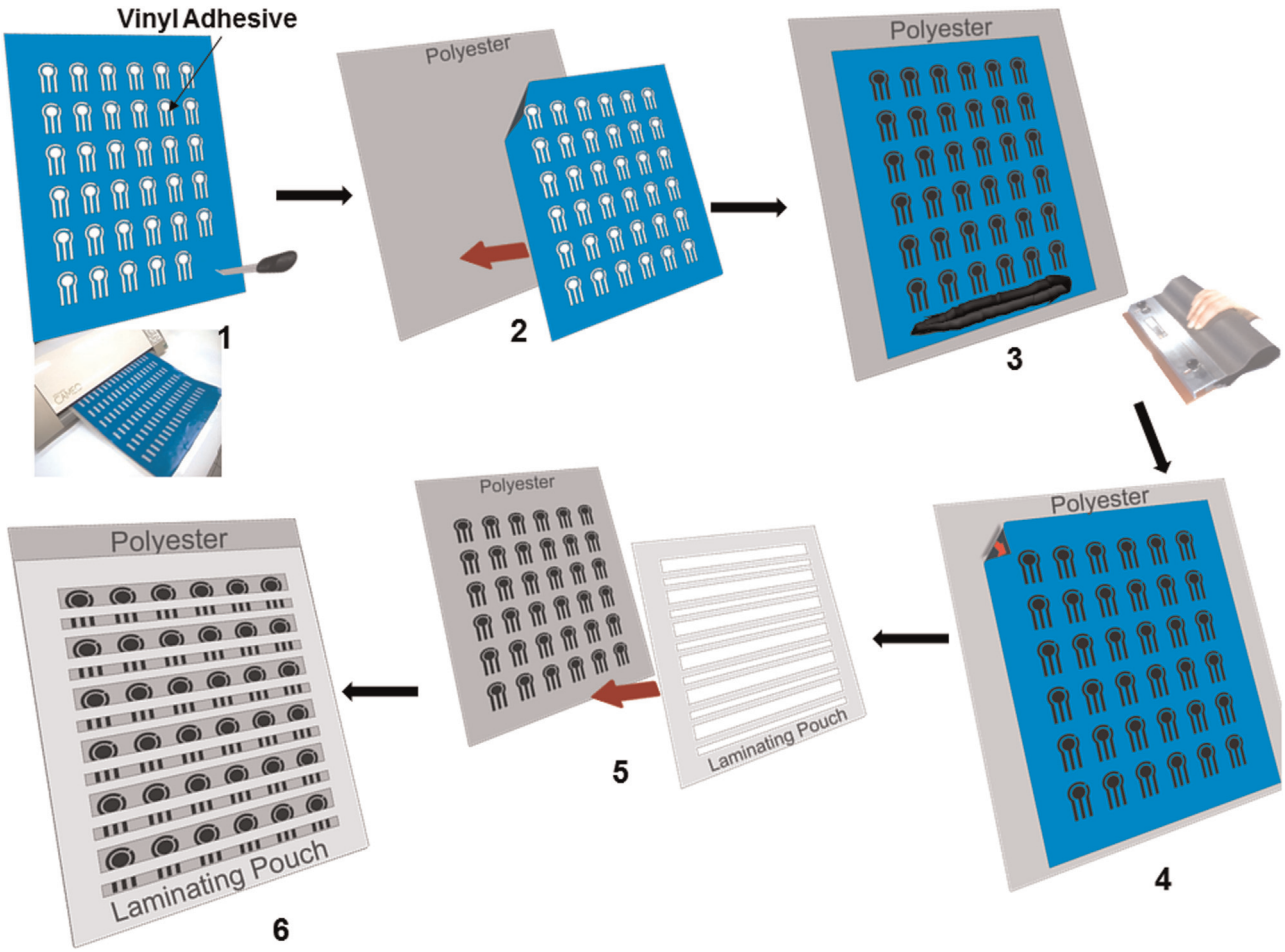

Fig. 1. Schematic representation of DCell fabrication: (1) preparation of the template by cutting the adhesive vinyl; (2) transfer of the vinyl to the transparency sheet; (3) carbon ink screen-printing, followed by Ag/AgCl ink deposition; (4) removal of the adhesive vinyl; (5) positioning of the lamination pouch on the printed electrodes, following by heating and pressing; and (6) the DCell ready for use.

2.2. Instruments

All voltammetric experiments were performed using an electrochemical analyser (μstat 8000, DropSens, Spain) connected to a personal computer running Dropview 8400 software. SEM images were acquired using a Model DSM960 microscope (Carl Zeiss, Jena, Germany).

2.3. DCell fabrication

The DCell fabrication procedure is illustrated schematically in Fig. 1. The layout of the homemade all-plastic carbon electrodes, comprising a working electrode (WE), a pseudo-reference electrode (RE), and a counter electrode (CE), was drawn using Silhouette Studio v. 2.7.4 software. The pattern was transferred to an adhesive vinyl film using an electronic craft cutter (Silhouette Cameo, Silhouette America, Inc.). Undesired portions were peeled off using tweezers, leaving the template of the electrochemical cell as a negative mask. Next, the vinyl with the template was attached to a polyester sheet (transparency film for laser printers, purchased in a local market) with dimensions of 21.0 cm × 29.7 cm. The carbon ink was then transferred using a squeegee, in three steps. First, the carbon ink (C2030519P4, Gwent Electronic Materials Ltd., UK) was poured onto the top of the vinyl mask surface and dragged across the template using the squeegee, resulting in ink deposited onto the polyester sheet with an average thickness of 80 μm (Fig. 1). After curing the ink for 30 min at 60 °C, Ag/AgCl ink (C2051014P10, Gwent Electronic Materials Ltd., UK) as the pseudo-reference electrode was deposited using a brush and then cured for 30 min at 60 °C. The vinyl mask was then removed. Finally, a lamination process was used to define the geometric area and insulate the electrodes. This involved the use of a laminating pouch (purchased locally) consisting of a sheet of transparent polyester covered with a thin layer of polyethylene. The pouch was appropriately cut, using the cutting printer, and placed onto the polyester sheet with the screen-printed electrodes, followed by application of heat and pressure using a heater press.

3. Results and discussion

3.1. DCell fabrication and electrochemical characterization

The design of the DCells is illustrated in Fig. 2. The details of a single DCell are shown in Fig. 2A, and Fig. 2B illustrates the large-scale production of DCells. A design with eight individual DCells for use in multipotentiostats is presented in Fig. 2C. Fig. 3A shows a scanning electron micrograph of the electrode surface, revealing typical graphite ink morphology with a rough surface over the polyester sheet [17,18]. Vertical inspection by optical microscopy (Fig. 3B) revealed the uniform coverage and well-defined electrode geometry achieved using the adhesive vinyl template and laminating process.

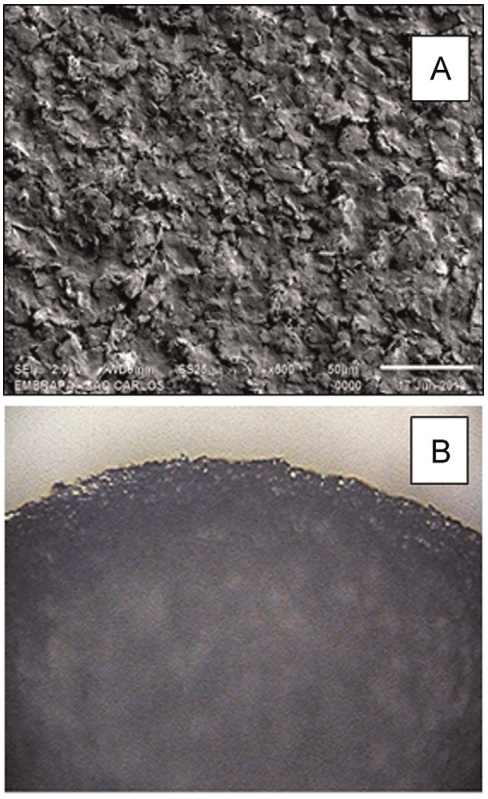

Fig. 3. (A) SEM images of the DCell working electrode (500 × magnification), (B) image of the DCell obtained using an optical microscope (20 × magnification).

The electrochemical performance of the DCells was evaluated by cyclic voltammetry (Fig. 4A). DCells with different working electrode geometries (diameters of 1.5, 2.0, and 3.0 mm) using ruthenium hexamine(III) chloride were evaluated in order to check the precision of the proposed construction method. The voltammograms revealed good electrochemical behaviour, with a potential difference between the reduction (E_{pc}) and oxidation (E_{pa}) peaks as well $E_p - E_p/2$ of 0.074 V and 0.046 V respectively, for all diameters using scan rates between 75 and 300 mV s^{-1}. Similarly, the anodic and cathodic peak current ratio (i_{pa}/i_{pc}) was close to 1.0. In addition, a linear trend was observed when the voltammetric anodic peak current (i_P) was plotted against the square root of the applied scan rate ($\upsilon^{1/2}$), over the range from 75 to 300 mV s^{-1} (Fig. 4B). This indicated that the rate of the reaction was governed by diffusion of the electroactive species to the surface of the electrode [17]. The electroactive areas of electrodes ($n=8$) determined using the Randles–Sevcik equation [17], with nominal diameters of 1.5, 2.0, and 3.0 mm were obtained as 1.59 ± 0.60, 2.65 ± 0.13, and 5.61 ± 0.16 mm^2, respectively. Relative standard

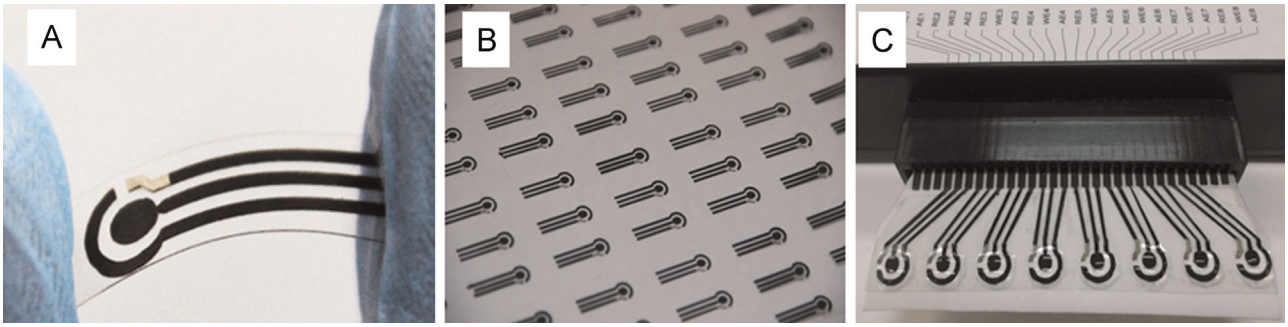

Fig. 2. Pictures of the DCells fabricated: (A) single DCell; (B) mass production of DCells; (C) eight Dcells for use in multipotentiostats.

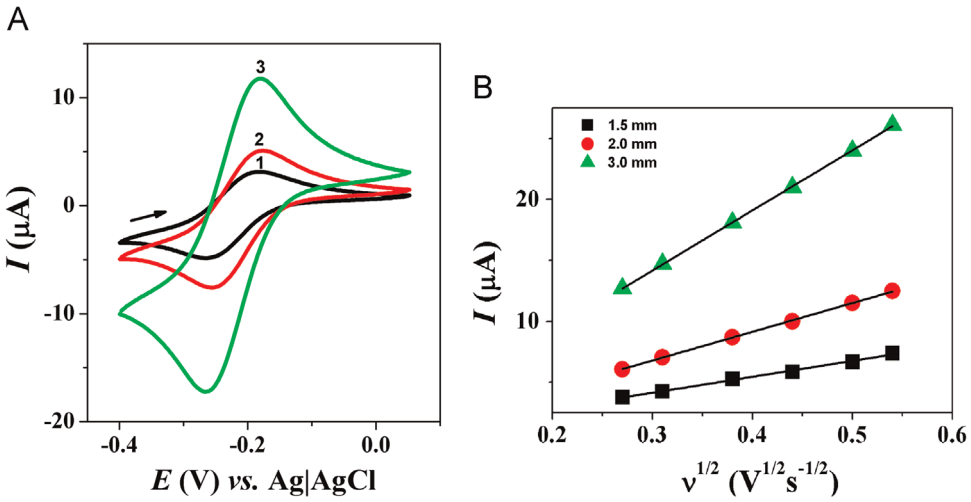

Fig. 4. (A) Cyclic voltammograms obtained in 1.0×10^{-3} mol L^{-1} ruthenium hexamine(III) in KCl (0.1 mol L^{-1}), using working electrodes with diameters of (1) 1.5, (2) 2.0, and (3) 3.0 (mm); scan rate of 100 (mV s^{-1}). (B) Plot of anodic peak current vs. the square root of the scan rate ($\upsilon^{1/2}$) for cyclic voltammetry experiments conducted with the DCell using 1.0×10^{-3} (mol L^{-1}) ruthenium hexamine(III) in KCl (0.1 mol L^{-1}).

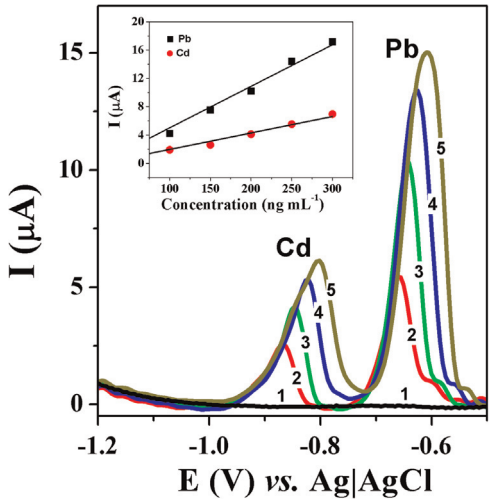

Fig. 5. Square wave anodic stripping voltammograms for concentrations of Cd and Pb ranging from 100 to 300 (ng mL^{-1}), in 0.1 mol L^{-1} acetate buffer (pH 4.5). The inset displays the corresponding calibration plot for Cd and Pb. Parameters: f=20 (Hz), ΔE_s=5 (mV), a=25 (mV), and deposition time=120 s at −1.2 (V). Curves 1–5: 0–300 (ng mL^{-1}).

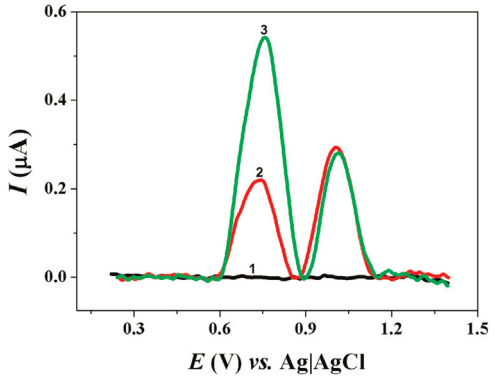

Fig. 6. Square wave voltammograms obtained using the unmodified electrode after interaction with bisphenol A (curve 1), the dsDNA-modified electrode without bisphenol A (curve 2), and the dsDNA-modified electrode after exposure to 1.0×10^{-5} (mol L^{-1}) bisphenol A for 60 (s) (curve 3). SWV conditions: f=100 (Hz), a=50 (mV), and ΔE_s=2 (mV).

deviations (RSD) ranging from 2.82% to 5.04% were indicative of good reproducibility of the developed DCell. The DCell was compared with a commercial screen-printed electrochemical cell from Dropsens (model DRP-8X110) and the voltammograms are shown in Figs. S1 and S2 in the Supplementary material. The DCell and the commercial screen-printed cell presented results with no statistical differences in terms of peak current density, with a 95% of confidence level.

A major advantage of our method is that the design and configuration of the electrodes can be easily modified, including single electrodes or arrays of electrodes. Furthermore, the technique is extremely cost-effective (in terms of materials, the cost is less than US $0.02 per electrochemical cell) and fast, requiring less than two hours for the construction of hundreds of DCells. The potential use of the DCells as sensors and biosensors was therefore evaluated as described below.

3.2. DCell applications

3.2.1. Electrochemical detection of cadmium and lead

The determination of heavy metals such as cadmium and lead is of considerable interest because these elements are important environmental pollutants [19]. They have no metabolic functions in most living organisms (with the exception of certain organisms under certain conditions), and their accumulation over time in animal tissues can cause serious illness [20]. Knowledge of their concentrations in various matrices is therefore necessary in order to safeguard human health [19]. Here, square wave anodic stripping voltammetry (SWASV) was used to evaluate the electrochemical performance of the DCell for simultaneous detection of Cd and Pb in water samples. The SWASV measurements were carried out in 0.1 mol L^{-1} acetate buffer solution (pH 4.5) containing Cd and Pb at concentrations ranging from 100 to 300 ng mL^{-1}. Convective accumulation of Cd and Pb on the DCell surface was carried out for 120 s at a deposition potential of −1.2 V, under magnetic stirring. Stripping of the DCell was then performed by scanning the potential from −1.2 V to −0.6 V using SWASV with frequency (f) of 20 Hz, step potential (ΔE_s) of 5 mV, and amplitude (a) of 25 mV [21].

Stripping voltammograms for increasing concentrations of Cd and Pb are shown in Fig. 5. Well-defined stripping peaks can be seen at −0.8 V and 0.6 V vs. Ag/AgCl, corresponding to Cd and Pb, respectively. When the Cd and Pb concentrations were increased (Fig. 5 inset), both peak currents increased linearly in the

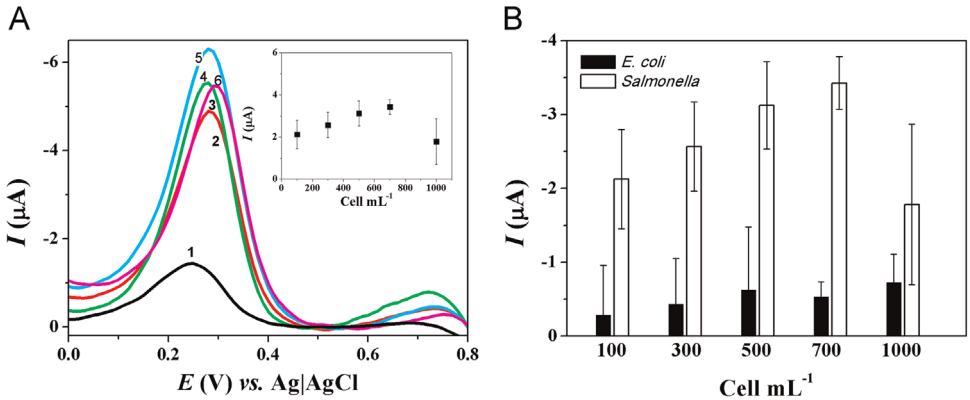

Fig. 7. (A) Differential pulse voltammograms obtained using electrochemical detection with the AuNPs: (1) immunoassay without *Salmonella*, (2) 100, (3) 300, (4) 500, (5) 700, and (6) 1000 bacteria (cells mL^{-1}). The inset displays the corresponding calibration plot. (B) Specificity study for immunoassays performed with *E. coli* or *Salmonella* at concentrations ranging from 100 to 1000 (cells mL^{-1}). Parameters: step potential 10 (mV), modulation amplitude 50 (mV), scan rate 33.5 (mV s^{-1}), and deposition time 120 (s) at +1.25 (V). The error bars show the standard deviations ($n=3$).

Table 1
Recovery studies of *Salmonella* levels in milk samples ($n=8$).

Sample	Added (cell mL^{-1})	Found (cell mL^{-1})	Recovery (%)
Milk	250.0	232.5 ± 0.2	93
	500.0	507.0 ± 0.1	101

concentration range studied. The calculated limits of detection (based on a signal-to-noise ratio (*S*/*N*) of three) were 50 and 39 ng mL^{-1} for Cd and Pb, respectively. The associated sensitivities and correlation coefficients were 25.96 μA/ng mL^{-1} and 0.996 for Cd, and 65.64 μA/ng mL^{-1} and 0.994 for Pb. Although higher sensitivity was achieved for the detection of Pb, compared to Cd, both metals could be measured at low levels. The results obtained with the unmodified DCell were comparable to those obtained in studies employing conventional screen-printed carbon electrodes and, similarly, the DCell could be improved by modifying the carbon surface with a thin layer of mercury or bismuth [21,22]. The DCell was therefore shown to be suitable for use as a chemical sensor for the determination of trace metals in water samples.

3.2.2. *Electrochemical study of the interaction of bisphenol A and DNA*

The DCell was used to study the interaction between bisphenol A and DNA. Electrophilic substances derived from endogenous and exogenous sources can modify the DNA molecule, causing damage. Significant deviations from the normal double helix structure can have an important impact on metabolic processes, since lesions may be mutagenic and contribute to the process of carcinogenesis [23,24]. For these analyses, the electrode surface was modified by DNA immobilization, as reported previously [25], i.e. the electrode surface was pretreated by applying +1.40 V for 300 s in 0.1 mol L^{-1} acetate buffer solution at pH 4.75 + 0.15 mol L^{-1} NaCl, followed by immersion for 180 s in a solution containing 0.5 mg mL^{-1} dsDNA, at a potential of +0.50 V (further details are presented in the Supplementary material). Square wave voltammograms were recorded using the DNA-modified electrode in the supporting electrolyte (0.1 mol L^{-1} acetate buffer solution at pH 4.75 + 0.15 mol L^{-1} NaCl, free of dsDNA), before and after immersion for 60 s in acetate buffer containing 1.0×10^{-5} mol L^{-1} bisphenol A followed by rinsing with H_2O for 30 s. The oxidation current intensities obtained for the guanine and adenine moieties after immersion were compared with the values obtained prior to the interaction [26,27]. All experimental curves were first baseline-corrected using application of a moving average with a step window of 5 mV (included in the GPES version 4.9 software). This mathematical treatment improves the visualization and identification of the DNA oxidation peaks [25].

Fig. 6 presents the square wave voltammograms for the unmodified electrode after immersion in bisphenol A followed by rinsing with H_2O (line 1), and for the dsDNA-modified DCell before (line 2) and after (line 3) interaction with bisphenol A. The voltammograms were acquired in 0.1 mol L^{-1} acetate buffer solution (pH 4.75) containing 0.15 mol L^{-1} NaCl. It was noted that bisphenol A did not adsorb directly on the electrode surface, since no oxidation peak was detected. The voltammogram for immobilized dsDNA presented two oxidation peaks, at potentials of +0.74 V and +1.01 V, corresponding to guanine and adenine moieties, respectively. The peak currents for dsDNA measured using 10 different DCells resulted in RSD values of 5.6% and 7.2% for the guanine and adenine residues, respectively, indicating excellent reproducibility of the dsDNA-modified electrode. It can be observed from Fig. 6 (line 3) that the voltammetric response for guanine increased approximately 2.5-fold, while there was no change in the adenine moiety current intensity after interaction with bisphenol A. No shifts in the peak potentials were observed for either of the base residues. The interaction study was performed using five independent modified electrodes and presented RSD values of 5.7% and 3.8% for the guanine and adenine residues, respectively. Changes in the guanine oxidation signal could be

Table 2
Comparison of *Salmonella* biosensors.

Sample	Biosensor configuration	Range	LOD	Ref.
Milk	Antigen–antibody – labelled with HRP	1–10^7 CFU mL^{-1}	7.5×10^{-3} CFU mL^{-1}	[33]
Not specified	DNA hybridization – detection with ruthenium complex	5–30 μM	0.208 μM	[34]
Chicken meat	Antigen–antibody – labelled with HRP	10^1–10^7 CFU mL^{-1}	20 CFU mL^{-1}	[35]
Not specified	Antigen–antibody – detection by EIS[a]	Not specified	500 CFU mL^{-1}	[36]
Pork meat	Aptamer – detection by EIS[a]	2.4–2.4×10^3 CFU mL^{-1}	3 CFU mL^{-1}	[37]

[a] EIS – Electrochemical Impedance Spectroscopy.

caused by distortions of the DNA double helix, since damage to the DNA base residues can result in local perturbations in the dsDNA structure, leading to rearrangement of DNA on the electrode and greater exposure of guanine bases to oxidation [28,29]. The damaged DNA provided greater contact of the guanine bases with the electrode, hence increasing their availability for oxidation after the interaction with bisphenol A. However, this process did not affect the electrochemical behaviour of the adenine moiety, indicating that bisphenol A showed a preference for interaction sites.

We therefore demonstrated that the disposable DCell can be successfully modified with DNA and applied in studies of interaction between bisphenol A and DNA molecules.

3.2.3. Electrochemical detection of salmonella

The bacterium *Salmonella* is the cause of salmonellosis, which is one of the commonest and most widespread food-borne diseases. In humans, the symptoms of salmonellosis are usually mild, although the illness can cause death in young children and the elderly. The classical culture assay is the method recommended by international health agencies to detect the microorganism. However, this procedure requires skilled technicians, pretreatment of the sample, and at least three days for results to be available. New technologies are therefore needed that can offer faster, simpler, and less expensive detection of *Salmonella* in food [30].

In order to demonstrate the ability of the DCell for the electrochemical detection of *Salmonella*, the use of gold nanoparticles (AuNPs) was evaluated [31]. Assays involving capture with magnetic beads (MBs), as well as the synthesis and modification of AuNPs used as labels, were conducted as reported previously [32]. The assays were carried out using 500 μL of different concentrations (100–1000 cells mL^{-1}) of dead *Salmonella* cells in PBS-Tween solution. The mixture was incubated with MBs modified with anti-*Salmonella* polyclonal primary antibody (MBs-pSAb). After separation and washing, the material was resuspended with AuNPs modified with anti-*Salmonella* monoclonal primary antibody (AuNPs-sAb), forming a MBs-pSAb/S/AuNPs-sSAb complex. The complex was separated, washed, and resuspended in PBS buffer. Aliquots of 10 μL of the solution containing the complex and 50 μl of 0.1 mol L^{-1} HCl were dripped onto the DCell surface and a magnetic field was applied below the working electrode. For electrochemical detection, a preconcentration process to oxidize the AuNPs to $AuCl_4^-$ was performed at +1.25 V vs. Ag/AgCl for 120 s. Immediately after the electrochemical oxidation, differential pulse voltammetry (DPV) was performed by scanning from +1.25 to 0 V (step potential 10 mV, modulation amplitude 50 mV, scan rate 33.5 mV s^{-1}). Fig. 7A displays the linear increase in the peak height for reduction of $AuCl_4^-$ ions over the analytical range from 100 to 700 cells mL^{-1}. The limit of detection (based on $S/N=3$), sensitivity, and correlation coefficient values were 100 cells mL^{-1}, 0.432 μA/cell mL^{-1}, and 0.983, respectively. The sensitivity obtained was better than previously published [32] methods and can be attributed to the good quality of the DCell as well as to the smaller size of MBs used in this work (1.8 μm vs. 3.2 μm) and the high sensitivity of the anti-*Salmonella* monoclonal antibody used.

The specificity of the magneto-immunoassay was further investigated in experiments to evaluate the response to the *Salmonella* in the presence of *E. coli* as a possible interferent (Fig. 7B). As expected, the signal for *E. coli* was almost 85% lower than the signal for *Salmonella* in the concentration range from 100 to 700 cells mL^{-1}. This level of interference could be explained by a degree of cross-reactivity and non-specific binding of the antibody used. However, this did not affect the ability to detect Salmonella. Furthermore, in order to determine the accuracy of the proposed immunosensor, skimmed milk purchased in local market was spiked with *Salmonella* at different concentrations. Good recoveries values for *Salmonella* was obtained in the range between 93% and 101% as can be seen in Table 1. These results demonstrate that the developed DCell could be a promising alternative to determine Salmonella in skimmed milk presenting a good limit of detection when compare with other methods in the literature as can be seen in Table 2. The DCell was therefore suitable for rapid, specific, and accurate detection of *Salmonella* using magneto-immunoassays.

4. Conclusion

A fast and cost-effective prototyping process was developed for the fabrication of all-plastic disposable carbon-based electrochemical cells. Use of a low-cost electronic craft cutter and a simple laminating process enabled hundreds of inexpensive electrochemical cells to be manufactured in less than two hours. The DCell was successfully used in sensor and biosensor applications and showed excellent performance. The new proposed prototyping process opens up new avenues for the development of disposable electrochemical devices for applications as sensors and biosensors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2015.09.002.

References

[1] N. Thiyagarajan, J.-L. Chang, K. Senthilkumar, J.-M. Zen, Electrochem. Commun. 38 (2014) 86–90.
[2] R.O. Kadara, N. Jenkinson, C.E. Banks, Electrochem. Commun. 11 (2009) 1377–1380.
[3] J.P. Metters, R.O. Kadara, C.E. Banks, Analyst 136 (2011) 1067–1076.
[4] M. Li, Y.-T. Li, D.-W. Li, Y.-T. Long, Anal. Chim. Acta 734 (2012) 31–44.
[5] K. Grennan, A.J. Killard, M.R. Smyth, Electroanalysis 13 (2001) 745–750.
[6] M. Singh, H.M. Haverinen, P. Dhagat, G.E. Jabbour, Adv. Mater. 22 (2010) 673–685.
[7] B. Weng, R.L. Shepherd, K. Crowley, A.J. Killard, G.G. Wallace, Analyst 135 (2010) 2779–2789.
[8] C.E. Krause, B.A. Otieno, A. Latus, R.C. Faria, V. Patel, J.S. Gutkind, J.F. Rusling, Chemistryopen 2 (2013) 141–145.
[9] R.P. Tortorich, E. Song, J.-W. Choi, J. Electrochem. Soc. 161 (2014) B3044–B3048.
[10] L. Huang, Y. Huang, J. Liang, X. Wan, Y. Chen, Nano Res. 4 (2011) 675–684.
[11] J. Jang, J. Ha, J. Cho, Adv. Mater. 19 (2007) 1772–1775.
[12] P.P. de Santana, I.M. Ferreira de Oliveira, E. Piccin, Electrochem. Commun. 16 (2012) 96–99.
[13] C.W. Foster, J.P. Metters, C.E. Banks, Electroanalysis 25 (2013) 2275–2282.
[14] R.S.P. Malon, K.Y. Chua, D.H.B. Wicaksono, E.P. Corcoles, Analyst 139 (2014) 3009–3016.
[15] P.K. Yuen, V.N. Goral, Lab Chip 10 (2010) 384–387.
[16] A.C. Glavan, R.V. Martinez, E.J. Maxwell, A.B. Subramaniam, R.M.D. Nunes, S. Soh, G.M. Whitesides, Lab Chip 13 (2013) 2922–2930.
[17] R.O. Kadara, N. Jenkinson, C.E. Banks, Sens. Actuators B 138 (2009) 556–562.
[18] J.P. Metters, S.M. Houssein, D.K. Kampouris, C.E. Banks, Anal. Methods 5 (2013) 103–110.
[19] G. Aragay, J. Pons, A. Merkoci, Chem. Rev. 111 (2011) 3433–3458.
[20] T.W. Lane, F.M.M. Morel, Proc. Nat. Acad. Sci. USA 97 (2000) 4627–4631.
[21] M.A. Granado Rico, M. Olivares-Marin, E. Pinilla Gil, Talanta 80 (2009) 631–635.
[22] I. Palchetti, A. Cagnini, M. Mascini, A.P.F. Turner, Mikrochim. Acta 131 (1999)

65–73.
[23] A. Oliveira-Brett, L. da Silva, Anal. Bional. Chem. 373 (2002) 717–723.
[24] V.C. Diculescu, A.-M.C. Paquim, A.M.O. Brett, Sensors 5 (2005) 377–393.
[25] C.V. Uliana, G.S. Garbellini, H. Yamanaka, Sens. Actuators B 178 (2013) 627–635.
[26] B. Meric, K. Kerman, D. Ozkan, P. Kara, M. Ozsoz, Electroanalysis 14 (2002) 1245–1250.
[27] M. Ozsoz, A. Erdem, D. Özkan, P. Kara, H. Karadeniz, B. Meric, K. Kerman, S. Girousi, Bioelectrochemistry 67 (2005) 199–203.
[28] E. Fuente, G. Villagra, S. Bollo, Electroanalysis 19 (2007) 1518–1523.
[29] M. Fojta, Detecting DNA damage with electrodes, in: E. Palecek, F. Scheller, J. Wang (Eds.), Perspectives in Bioanalysis, Elsevier, Amsterdam, 2005, pp. 385–431.
[30] A. Ahmed, J.V. Rushworth, N.A. Hirst, P.A. Millner, Clin. Microbiol. Rev. 27 (2014) 631–646.
[31] J.M. Pingarrón, P. Yáñez-Sedeño, A. González-Cortés, Electrochim. Acta 53 (2008) 5848–5866.
[32] A.S. Afonso, B. Perez-Lopez, R.C. Faria, L.H.C. Mattoso, M. Hernandez-Herrero, A. Xavier Roig-Sagues, M. Maltez-da Costa, A. Merkoci, Biosens. Bioelectron. 40 (2013) 121–126.
[33] S. Liébana, A. Lermo, S. Campoy, M.P. Cortés, S. Alegret, M.I. Pividori, Bionsens. Bioelectron. 25 (2009) 510–513.
[34] T. García, M. Revenga-Parra, L. Añorga, S. Arana, F. Pariente, E. Lorenzo, Sens. Actuators B 161 (2012) 1030–1037.
[35] F. Salam, I.E. Tothill, Biosens. Bioelectron. 24 (2009) 2630–2636.
[36] V. Nandakumar, J.T. La Belle, J. Reed, M. Shah, D. Cochran, L. Joshi, T.L. Alford, Biosens. Bioelectron. 24 (2008) 1039–1042.
[37] X. Ma, Y. Jiang, F. Jia, Y. Yu, J. Chen, Z. Wang, J. Microbiol. Methods 98 (2014) 94–98.