A printed electrocatalyst for hydrogen peroxide reduction

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ABSTRACT

The modification of silver screen-printed electrodes with a dodecyl benzenesulphonic acid and KCl solution was performed by inkjet printing. Scanning Electron Microscopy was performed to characterize the electrode surfaces. Electrochemical reduction of H_2O_2 was studied and compared to electrodes modified by dip-coating. Analytical parameters of the all-printed electrode such as LOD, sensitivity and inter-electrode reproducibility were calculated (5.8×10^{-6} M, 4.9×10^{-2} $AM^{-1}cm^{-2}$ and approx. 10%) and contrasted with other data in the literature for the measurement of H_2O_2. Ink jet printing led to reductions in required surface modification times and improved signal to background levels and reproducibility.

Keywords

Inkjet printing; Hydrogen peroxide; Silver; Dodecylbenzene sulphonic acid

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The detection of hydrogen peroxide has shown to be very important in recent years due to its relevant role in many industrial applications as well as biological reactions.[1-7] Recently, traditional techniques for H_2O_2 detection (e.g. titrimetry,[8] spectrophotometry[9] and chemiluminescence[10, 11]) have been replaced by electrochemical methods because they are rapid, low cost and easy for automation detection.[4, 5] Many metal and metal alloys such as Pt,[6, 12] Pd,[13] Ag,[14] Pd/Au[15] and Au/Pt[5] have been employed in the manufacture of electrochemical sensors for H_2O_2 determination. Recently, an enhancement of the catalytic activity of silver screen-printed electrodes towards H_2O_2 reduction after electrode exposure to a mixed solution of dodecyl benzenesulphonic acid (DBSA) and KCl has been reported.[16] The mixed surfactant/salt modification solution brought about changes in both the morphology and chemical composition of the silver paste electrode surface, which improved the electrochemical reduction of H_2O_2 at -0.1 V vs. Ag/AgCl up to 80-fold on such material.

Screen-printing technique has been widely used for large-scale manufacture of disposable sensors because of its low cost, speed and easy-to-operate characteristics.[17-19] During the printing process, a liquid paste is forced through a mesh screen to form a pattern onto a substrate surface.[18, 19] Generally, screen-printing has been used for the fabrication of the electrode materials and further modifications such as biomolecule deposition are performed by other techniques.[20-22]

Inkjet printing has proven to be a very promising technique capable of manufacturing low cost electronic sensor platforms. It allows the deposition of very small volumes of ink (picolitres) on a substrate (glass, plastic, metal, ...) in a rapid procedure, achieving high pattern precision and resolution.[18, 19] One of the most common inkjet printers is based on the drop-on-demand piezoelectric printhead, which permits the ejection of tiny droplets ($\geq$ 1 pl) after the application of an electrical field across the piezoelectric material confined within the nozzle.[23, 24]

In the present work, a fully printed electrocatalyst for H_2O_2 reduction was managed using a screen-printed silver electrode as a platform and a DBSA/KCl inkjet printed layer to enhance the sensing properties of the material on H_2O_2. The use of inkjet printing might improve the variability of the sensing devices found in previous manual modification procedures by enhancing the control of the reagent volume and exposure times. Cyclic voltammetry and amperometry were performed to compare the catalytic activity on H_2O_2 reduction of electrodes modified by both inkjet printing and manual dip-coating techniques.

Fig. 1A shows the cyclic voltammograms for unmodified, dip-coated DBSA/KCl modified and inkjet printed DBSA/KCl modified silver paste electrodes in the absence of H_2O_2.

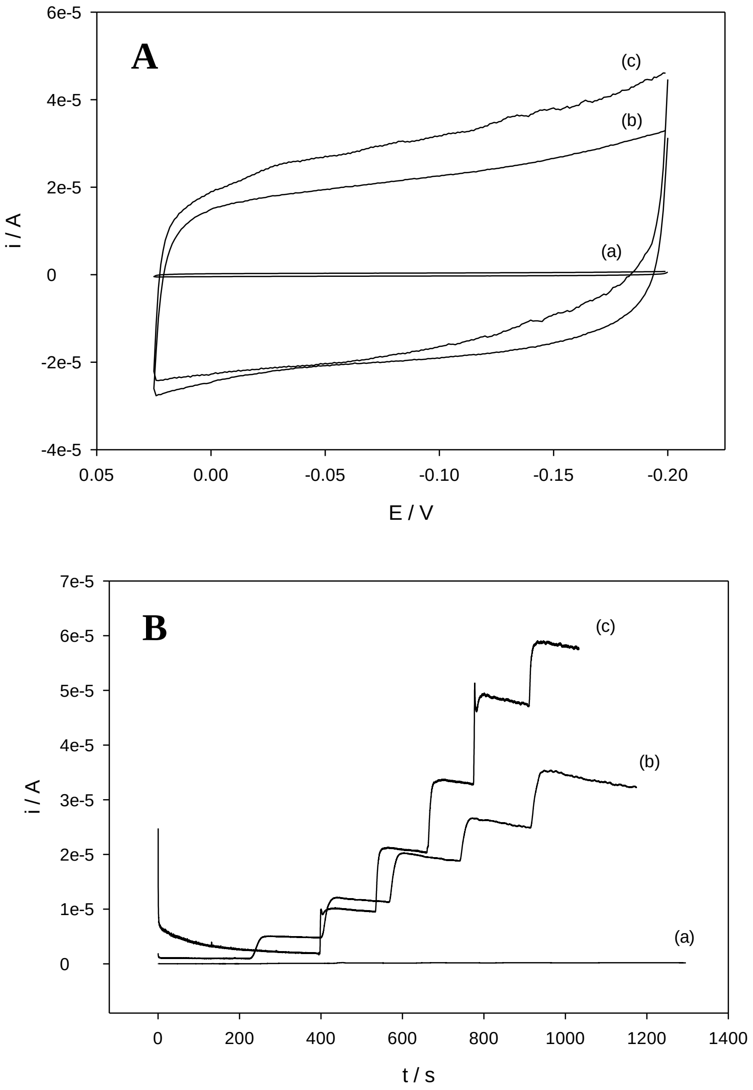

Figure 1. **(A) Cyclic voltammograms measured in PBS pH 6.8 solution, in the absence of H_2O_2 and (B) Amperometric responses measured at –0.1 V (vs Ag/AgCl) in PBS pH 6.8, at H_2O_2 concentration from 1 to 5 x 10^{-3} M, of silver paste electrodes: (a) unmodified; (b) 3.3 x 10^{-2} M DBSA/ 0.1 M KCl modified by inkjet printing and (c) 3.3 x 10^{-2} M DBSA/ 0.1 M KCl modified by dip-coating.**

As can be observed, the non-faradaic or charging current from the cyclic voltammograms was much higher for the modified electrodes than for the unmodified one, indicating that the silver paste electrodes had undergone a surface modification after immersion into the surfactant/salt solution. This phenomenon has been reported previously.[16] Typical amperometric responses at -0.1 V (vs Ag/AgCl) for the unmodified and DBSA/KCl modified electrodes in H_2O_2 are shown in Fig. 1B. The cathodic currents exhibited by the unmodified, dip-coated and inkjet printed DBSA/KCl modified electrodes in the presence of 5 x 10^{-3} M H_2O_2 were 1.7 x 10^{-7} A, 5.6 x 10^{-5} A and 3.1 x 10^{-5} A, respectively. Therefore, inkjet printed DBSA/KCl modified electrodes underwent a surface modification which led to an enhancement in its catalytic activity towards H_2O_2 reduction. The modification time was remarkably reduced by the inkjet printing process (from 3 h to 10 min). Moreover, the initial charging current and the background current were lower for the electrode modified by inkjet printing, as well as reaching steady state more quickly.

Also, scanning electron micrographs of silver paste electrodes modified by both techniques, before and after H_2O_2 sensing were carried out and are shown in Fig. 2. The spheroidal structures observed on electrode surfaces following DBSA/KCl modification by dip-coating (2C) were not clearly evident on the electrode surfaces modified by inkjet printing (2B). At first, silver screen-printed electrodes modified by inkjet printing exhibited electrode surfaces analogous to the unmodified electrode (2A). Moreover, the morphology of the spheroidal structures appeared to change following the H_2O_2 sensing process (2E). Such variation in the structures might be explained by a possible interaction between H_2O_2 and the structures during the reduction process. However, electrodes modified by inkjet printing did not present any apparent change after H_2O_2 catalysis although they still showed a noticeable enhancement on H_2O_2 reduction with respect to the unmodified electrodes. Two possible phenomena might explain such different surface characteristics and catalytic activities of the inkjet printed modified electrodes: the volume of DBSA/KCl that the surface is actually exposed to and the deposition technique itself. Although increasing voltages did not seem to make catalysis worse, maybe catalysis was already impacted even at low voltages. On the other hand, the driving force of the modification adsorption process may still not be as effective when performed in smaller volumes. Therefore, it might be assumed that the phenomenon is not different, but more limited and harder to visualize when DBSA/KCl is deposited by inkjet printing.

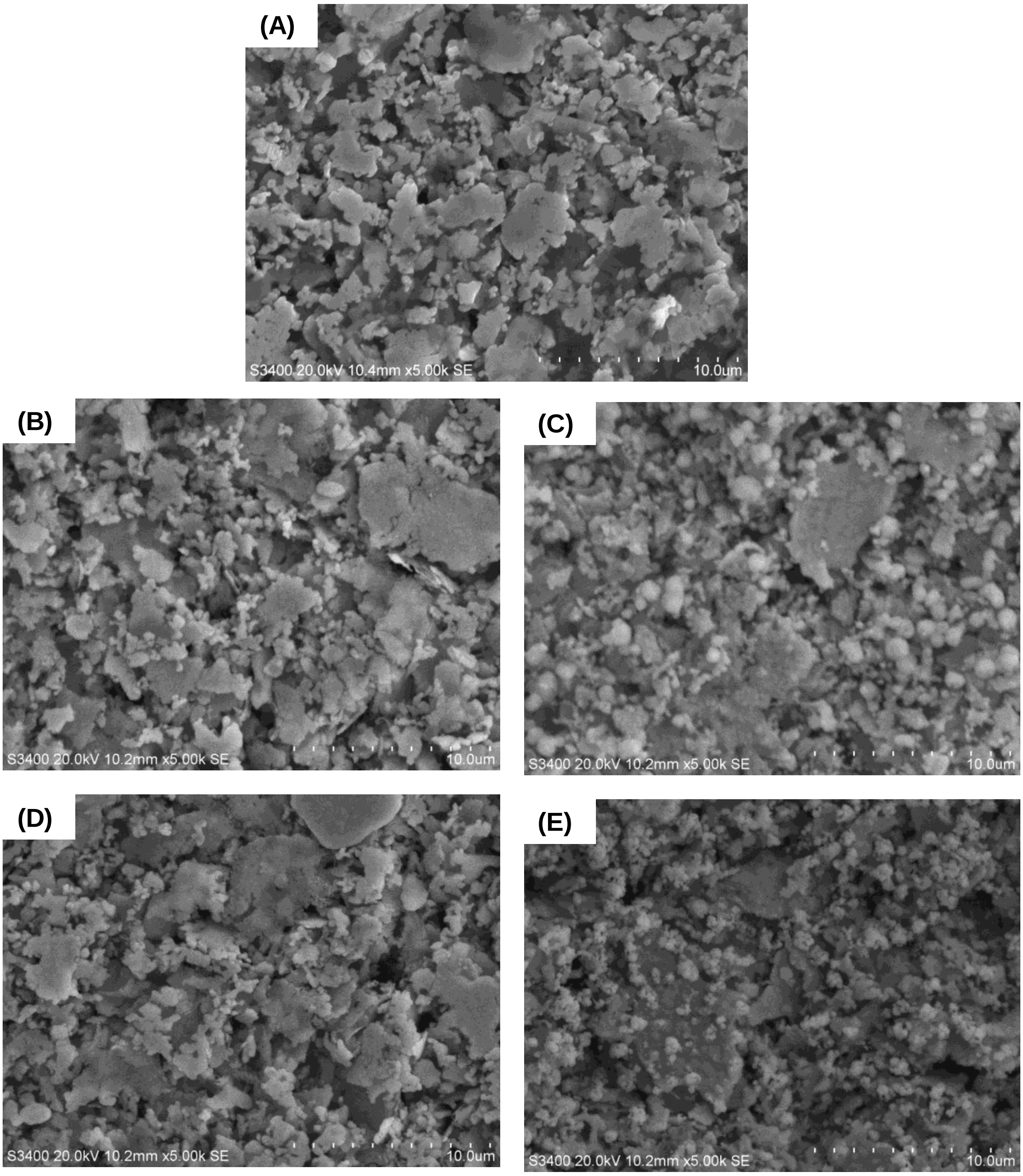

Figure 2. **SEM images using secondary electron (SE) detection of silver screen-printing electrodes (A) unmodified; (B) DBSA/KCl modified by inkjet printed, before H_2O_2; (C) DBSA/KCl modified by dip-coating, before H_2O_2; (D) DBSA/KCl modified by inkjet printed, after electrochemical reduction of 5×10^{-3} M H_2O_2 and (E) DBSA/KCl modified by dip-coating, after electrochemical reduction of 5×10^{-3} M H_2O_2. Accelerating voltage of 20 kV. (5.0k x magnification).**

Inkjet printing parameters such as ejection volume, solution concentrations and nozzle voltage were subsequently optimised. The mass of modifying agent that is deposited is a combination of the concentration and the volume of liquid per unit area that can be deposited, which is in turn dependent on the contact angle of the liquid on the surface. One of the ways of increasing the mass of modification solution that the surface is exposed to is to increase the number of prints, assuming that the concentration remains constant. The optimum number of prints was assessed by amperometry, contrasting the catalytic response towards H_2O_2 of the electrodes modified with a 3.3×10^{-2} M DBSA/ 0.1 M KCl solution. The average and standard deviation for the cathodic currents are shown in Table 1.

Table 1. Optimization data for inkjet printing parameters.

EJECTION VOLUME		DBSA CONCENTRATION		KCl CONCENTRATION		NOZZLE VOLTAGE	
Nº prints	$i_{cat\ 5mM\ H2O2}$/ A	[DBSA] / M	$i_{cat\ 5mM\ H2O2}$/ A	[KCl] / M	$i_{cat\ 5mM\ H2O2}$/ A	Nozzle Voltage/V	$i_{cat\ 5mM\ H2O2}$/ A
0	7×10^{-7}	3.3×10^{-3}	1.08×10^{-5}	0.004	2.6×10^{-6}	10	8×10^{-7}
1	$1.91x10^{-5}$	1.67×10^{-2}	1.52×10^{-5}	0.04	1.99×10^{-5}	13	$2.48x10^{-5}$
5	$3.41x10^{-5}$	3.30×10^{-2}	1.86×10^{-5}	0.1	3.11×10^{-5}	16	$3.57x10^{-5}$
10	$2.30x10^{-5}$	6.70×10^{-2}	1.59×10^{-5}	0.12	2.52×10^{-5}	20	$3.17x10^{-5}$
15	$2.67x10^{-5}$					25	$3.28x10^{-5}$
20	$2.26x10^{-5}$					30	$3.85x10^{-5}$

As can be observed, one print of surfactant-based solution onto Ag SPEs was enough to enhance the catalytic response of the electrodes. Such a response seemed first to increase from 1 to 5 prints and then decrease above this. A possible explanation might be related to the amount of DBSA/KCl solution required for the modification. The adsorption of the DBSA/KCl to the electrode surface would follow an adsorption isotherm. The volume of modification solution on the electrode surface would act as a reservoir from which DBSA/KCl is adsorbed. This would then deplete the solution of DBSA/KCl. It would appear that five prints allowed sufficient adsorption of DBSA/KCl to the electrode to result in its complete modification. Above this, this effect was either not apparent, or actually slightly reduced the performance of the electrode due, possibly, to inhibitory concentrations of the modification material. Thus, five prints of the surfactant-based solution (equivalent to 1.0 x 10^{-8} l) seemed to be optimum to achieve the highest enhancement in H_2O_2 catalysis.

The concentrations of DBSA and KCl in the inkjet printing modification solution were then assessed by using 3.3 x 10^{-2} M DBSA over a range of KCl concentrations followed by 0.1 M KCl over a range of DBSA concentrations. The cathodic responses to 5 x 10^{-3} M H_2O_2 were correlated with DBSA or KCl concentrations. The responses of silver screen-printed electrodes after five prints of the corresponding modification solution are shown in Table 1. As can be observed, the catalytic effect on H_2O_2 reduction increased with both DBSA and KCl concentration in the modification solution to be printed, with optimum values reached at 3.3 x 10^{-2} M DBSA and 0.1 M KCl. These data further suggest that the DBSA/KCl structures survive the inkjet printing process, at least to a significant degree.

Nozzle voltage can also influence the level of catalytic activity by affecting the actual voltage felt by the modification solution and the volume of deposited material.[25, 26] The effect of the nozzle voltage on H_2O_2 catalysis was evaluated by applying several nozzle voltages during the DBSA/KCl inkjet printing modification process (Table 1). No changes in the catalytic response were observed when the exposure time following printing was assessed. A voltage of 10 V was not strong enough to cause the ejection of the solution and so, therefore, did not show any catalysis. Little change in catalytic current was observed between 13 and 30 V suggesting that nozzle voltage did not have any effect on the formation of the catalytic surface. The difference observed between techniques might imply that the application of any voltage, even 13 V, to DBSA/KCl solution already has an effect on it, leading to the 1.2-fold reduction in catalysis observed.

Therefore, five prints (1.0 x 10^{-8} l), 3.3 x 10^{-2} M DBSA/ 0.1 M KCl and 16 V nozzle voltage seemed to be the optimal parameters for DBSA/KCl modification of silver paste electrodes by inkjet printing. A calibration curve for the all-printed H_2O_2 sensor was performed and analytical parameters such as sensitivity and reproducibility were calculated and compared to the dip-coated ones (Table 2). The DBSA/KCl modified electrodes prepared by dip-coating showed consistently higher catalytic responses towards H_2O_2 reduction and lower LOD than those electrodes treated by inkjet printing. One possible explanation might be an as yet identified impact that inkjet printing technique has on the DBSA/KCl solution. Nozzle voltages higher than 13 V led to DBSA/KCl deposition but it might be in some measure altered after the printing process, bringing about a different behaviour of the modified electrodes towards H_2O_2 reduction. In previous work, the catalytic enhancement observed on silver screen-printing electrodes after DBSA/KCl treatment was partially attributed to the interaction of micellar/lamellar structures from the solution with the screen printed electrode surface.[16] If the printing process affected the structure of the modification solution, that would change its catalytic effect and would diminish the catalytic enhancement towards H_2O_2.

Table 2. Analytical parameters for H_2O_2 sensors prepared by dip-coating and inkjet printing

	Dip-coating	**Inkjet printing**
Sensitivity / $AM^{-1}cm^{-2}$	8.1×10^{-2}	4.9×10^{-2}
LOD[1] / M	1.2×10^{-6}	5.8×10^{-6}
Reproducibility	~ 10%	~ 10%

[1] LODs were calculated at S/N=3 H_2O_2 concentration ranges from 1.25 to 2.25×10^{-4} M

Regarding the variability of the modification methods, both techniques exhibited similar relative reproducibility in the measurements, with an average value of 10% in both cases. These reproducibility and sensitivity values were in line with data reported in the literature for other modified screen printed electrodes for the detection of H_2O_2.[27-29]

Therefore, inkjet printing turned out to be a suitable technique for the deposition of DBSA/KCl solution on silver paste electrodes. Printing parameters such as volume ejected, DBSA and KCl concentrations in the solution and nozzle voltage were optimized. The all-printing H_2O_2 sensors showed a sensitivity of 4.9×10^{-2} $AM^{-1}cm^{-2}$ and a reproducibility of approx. 10%, which seemed to be in agreement with other systems found in the literature. The possibility of a potentially negative impact of the voltage applied during the printing process, together with the smaller volumes of modification solution in contact with the electrode surface may explain the differences found respect to the electrodes modified by dip-coating.

Experimental

Dodecylbenzenesulfonic acid (DBSA-D0989) was purchased from TCI Europe. Sodium and potassium chloride (NaCl, KCl), potassium dihydrogen phosphate (KH_2PO_4) and pbenzoquinone (BQ) were purchased from Sigma-Aldrich. Di-sodium hydrogen phosphate (Na_2HPO_4) was purchased from Riedel-de Haen. 30% (v/v) hydrogen peroxide solution was purchased from Merck. Silver conductive ink (Electrodag® PF-410) was purchased from Henkel (Scheemda, The Netherlands). Poly(ethylene) terephthalate substrates were Melinex® (pre-shrunk) films obtained from HiFi Industrial Film Ltd. (Dublin, Ireland). All the solutions were prepared using 18 MΩ Milli-Q water.

Silver paste electrodes were fabricated according to Gonzalez-Macia et al.[16] For the surfactant/salt-based modification, either a solution of 3.3×10^{-2} M DBSA/ 0.1 M KCl was inkjet printed onto the silver screen-printed electrodes or the electrodes were dipped into the modification solution for 3 h. Inkjet printing was performed using a Dimatix Materials Printer DMP-2831 (FujiFilm Dimatix, Inc.) and a Dimatix Drop Manager DMP-2800 series software. The Dimatix cartridges used for printing were MEMs-based, with 16 nozzles (20 µm diameter) spaced at 254 µm. The droplet volume was quoted at being 10 pl. DBSA/KCl solution was inkjet printed by placing the freshly prepared solution at the corresponding concentration in a Dimatix cartridge. No prior filtering was performed in order to avoid any possible breaking-down of the micelle/lamellar structures created in the surfactant-based solution. Unless otherwise stated, the solution was printed onto the silver screen-printed electrodes using circular patterns (5.04 mm diameter) and 20 µm resolution (dot spacing), which was equivalent to approx. 1270 dpi (drops per inch). Electrodes were then rinsed to remove the excess of modification solution that did not interact with the electrode surface.

All electrochemical measurements were performed in a three-electrode electrochemical batch cell, using a Ag/AgCl/NaCl (saturated) electrode and a platinum mesh electrode as reference and auxiliary electrodes, respectively. Cyclic voltammetry and amperometry measurements were carried out with a CHI601C electrochemical analyzer with CHI601C software (IJ Cambria Scientific Ltd., UK). Measurements were performed at room temperature, 18 ± 2 °C. Unless otherwise stated, all potential values are referenced to the Ag/AgCl/NaCl (saturated) electrode. The electrodes were measured in 10 ml phosphate buffered saline solution (PBS) pH 6.8. The buffer solution was prepared as reported before.[16] Cyclic voltammograms were obtained in the potential range from -0.200 to 0.025 V (vs Ag/AgCl) at a scan rate of 0.1 V/s. Amperometry was performed at -0.1 V (vs Ag/AgCl). 1 M stock solution of hydrogen peroxide was prepared daily and then aliquots from this solution were added to the working cell during the electrochemical characterisation.

Scanning Electron Microscopy (SEM) using Secondary Electron (SE) detection was carried out with a Hitachi S-3400N. An acceleration voltage of 20 kV was used to obtain the surface images.

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