"Paper and Inks": Sustainable Sensing Through Development of Paper Platforms

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Abstract

The platform of biosensor plays a pivotal role in the efficacy of detection; therefore, the selection of an optimal material that meets all requisite criteria is essential. Paper as a platform for sensing application exhibit additive attributes over the other commercially available substrates as it might fulfils the 'REASSURED' benchmark introduced under WHO guidelines. The study entails the fabrication of an electrochemical biosensing platform using regular office paper with different GSM thickness (75, 85,120 and 140 GSM). The conductive inks, paper thickness, design pattern, hydrophobic layer and connection materials were iterated and optimized through multiple scans of cyclic voltammetry. A simplified design of three electrode system having reference and working electrode was optimized at a distance of around 1mm. The concentration and number of layers of conductive inks were optimized through conductivity measurements which lie between 1Ω to 4 Ω for reference electrode and 0.0005 MΩ to 0.025 MΩ for counter electrode. Working electrode was fabricated using two differently modified conductive CNTs ink where conductivity varied for PCNT as 0.06 kΩ to 0.1 kΩ while LCNT varied 0.014 kΩ to 1.33 KΩ. Beside this an ecofriendly volatile organic compound free hydrophobic reagents were also tested for fabricating the sensing region. The CV scans show stability of adsorbed conducting materials on the fabricated paper platform stating that the platform could be further evaluated for biosensing application.

Keywords: Paper platform, Carbon Nanotubes, ePADs, Electrochemical sensors, Cyclic Voltammetry.
Received 30 January 2025; First Review 21 February 2025; Accepted 19 March 2025.

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How to cite this article
Ayushi, Neha Agrawal, Niroj Kumar Sethy, "Paper and Inks": Sustainable Sensing Through Development of Paper Platforms, J. Cond. Matt. 2025; 03 (01): 120-125.

Available from:
https://doi.org/10.61343/jcm.v3i01.110

Introduction

Biosensor platforms are designed with diverse architectures for the precise detection of biomolecules. These platforms are critical for advancing diagnostic accuracy, therefore optimal material selection is crucial for high sensitivity, specificity, and rapid response time. Paper has been widely used as a fascinating substrate for the development of biosensors as it offers the promising avenues for point of care diagnostics, aligning the 'REASSURED' criteria providing a current advancement in health monitoring. 'REASSURED' stands for Real-time connectivity, Ease of specimen collection, Affordable, Sensitive, Specific, User-friendly, Rapid and robust, Equipment free or simple Environmentally friendly, Deliverable to end-user [1]. Paper-based analytical biosensors provide portability, reliability, rapid detection, and a sustainable, eco-friendly approach for various detection methods, including electrochemical, optical, and fluorescence techniques, facilitating the identification of biomolecules such as bacteria, viruses, neurotransmitters, glucose, and proteins [2]. Numerous researches have reported the use of various paper types, including whatman filter paper, office paper, wax-printed paper, and chromatography paper, in the fabrication of paper-based analytical devices (PADs) [3]. Each type of paper exhibits distinct characteristics, specifically optimized and tailored for particular sensor functions. Electrochemical paper based analytic devices (ePADs) involves coupling of paper based biosensor with the use of electrochemical methods such as cyclic voltammetry [4]. In recent years, carbon-based nanomaterials, including carbon nanotubes, graphene, and graphite, have been recognized for their distinctive physical and chemical properties, such as biocompatibility, electrical conductivity, and high surface area, which are leveraged as critical components in the formulation of conductive inks

for the fabrication of paper-based sensors [5]. For instance, carbon nanotube inks can be dispersed in a solvent and printed onto paper substrates, facilitating the development of electrochemical sensors [6] Additionally, graphene-based inks exhibit exceptional conductivity and mechanical attributes, rendering them highly promising for similar applications [7].

The aim of this study is to develop a paper-based platform for sustainable sensing, utilizing standard office paper, which is subsequently printed with an inkjet printer to fabricate the electrode design. Carbon nanotube ink is employed for the working electrode. The fabricated electrode is characterized by assessing its conductivity and morphology. Furthermore, the electrode design is optimized based on variables such as paper type, hydrophobic barriers, and connection materials through cyclic voltammetry.

Materials and Method

Chemicals and apparatus

Potassium Ferrocyanide ($K_4[Fe(CN)_6]$), 6 amino caproic acid (AHA), polystyrene sulfonate (PSS), KCl (Potassium Chloride), Carbon nanotubes (CNTs), Milli-Q water (Millipore), Phosphate buffer solution (PBS) at pH 7.0, Mineral oil, Doms wax crayons, Silver paste, Office paper (JK excel Bond & Lotus Ivory Sheets) A4 75, 85, 120, 140 gm^{-2}, Apsara graphite 6B pencil. MS word software is used for the electrode design. Two probe multimeter is used for measuring ohmic resistance. Electrochemical experiments were performed using a *Emstat4S palm-sens potentiostat* and PS Trace 5.9 software was used for scanning. All experiments were conducted at room temperature.

Fabrication and testing of paper platform

For electrode fabrication, four types of A4 office paper with thicknesses of 75, 85, 120, and 140 g/m^2 were used, with two design patterns as mentioned in Table 1 and Figure 1. Pristine MWCNTs were modified via sonication, stirring, centrifugation, and drying using 1% PSS and lithium salt of 6-amino caproic acid (AHA), yielding PCNT (PSS-modified CNT) and LCNT (AHA-modified CNT) [11]. The electrodes were constructed by layering graphite for the counter electrode, silver paste for the reference electrode, and PCNT as well as LCNT conductive ink (50ul) for the working electrode. Hydrophobic barriers were added using wax crayon by coloring and heating while immersed and travelled through capillary driven force in mineral oil.

Electrochemical measurements

Cyclic voltammetry was conducted with an initial potential range of -1.6 V to +1.6 V. The analysis began with 5 cycles to assess potential etching, followed by an extended 25-cycle evaluation to ensure stability.

Table 1: Geometrical dimensions of the paper-based electrode employed for fabrication.

Dimension	Dimension 1	Dimension 2
Total length of electrode	60mm x 40mm	49.99mm x 13mm
Clipping Box	3mm x 3mm	4.99 mm x 3.5 mm
WE Diameter	3mm	3mm
Distance between RE and WE	4mm	1mm
Surface Area of CE	81.2 mm^2	40.5476 mm^2

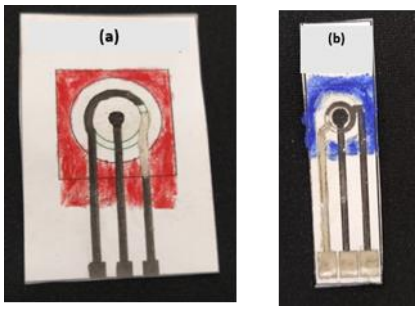

Figure 1: Paper electrodes were fabricated based on the specified dimensions, Dimension 1 (D1) and Dimension 2 (D2), as outlined in Table 1.

Each cycle was performed at a scan rate of 0.05 V/s with a step potential of 0.01 V. A 50 ul of 0.1M PBS solution served as the electrolyte for entire electrochemical reactions.

Results and Discussion

Investigation of modification of CNTs as conductive inks

For fabrication of paper electrodes investigation of interaction between platform and conductive inks is the primary step. The two biocompatible methods of CNTs modification, already explored for other applications are revisited over here to evaluate their conductivity henceforth utilized as conductive inks for ePADs [12-13]. The modification method of CNTs were optimized by varying various ratios and percentage of modifier (PSS and AHA).On basis of conductivity the most optimized concentration was chosen for further studies. We have restricted the use of modified CNTs as conductive inks only for working electrode to simplify the study with the purpose of understanding electrochemical interaction of ink with paper platform. The modified CNTs designated as LCNT for AHA salt modified CNTs and PCNT for PSS modified CNTs were chosen for the study. The reason behind the selection of such modifier was to deagglomerate pristine

CNTs in aqueous medium without usage of long chemical route and harsh chemicals. The two modifiers drew our attention due to their biocompatible nature, one being as FDA approved drug (AHA) while other as neuroactive agent (PSS). Both modifiers had ability to generate negative surface charge on being adsorbed through non covalent interaction keeping the carbon nanoform de-agglomerated and well dispersed in aqueous medium as well stated in earlier studies [14-16].

The morphological evidence of such modified CNTs were reported in our earlier work [17] which illustrated that the modified CNTs with AHA salt had been adsorbed on the surface of CNTs that had resulted in thickening of CNTs surface. Along with thickness of the wall, modified surface of CNTs were found rough and irregular in nature. This roughness and irregularity could be useful for ePADs fabrication as it could increase the electroactive area in contrast to unmodified CNTs or covalently modified CNTs which were often smoother compared to non-covalently modified surface.

Conductivity and Layer Optimization of Working, Counter and Reference electrodes on different papers type

The ohmic resistance of the conductive path is measured via two-point multimeter. The resistance measurements yielded crucial insights into the optimal deposition via concentration and number of depositing layers of conductive ink necessary to achieve sufficient conductivity on the electrodes. Moreover, for evaluating the reproducibility of the fabricated inks the electrical resistance of the electrode was tested so as to keep it similar among all designed electrodes. The average resistance value of counter, working and reference electrode is shown in figure 2 for the paper type of varied thickness. The graph indicates that LCNTs exhibit higher resistance than PCNTs, confirming PCNTs superior conductivity and higher current output potential for working electrodes as a conductive ink. The counter electrode was fabricated using a graphite layer via pencil friction due to its cost-effectiveness and simplicity, while the reference electrode utilized commercial silver paste, whose conductivity remained consistent across paper thicknesses ($p>0.05$, p value 0.2377). Although 75GSM paper showed significantly lower resistance ($p=0.003$) for the counter electrode which could be because of the easy penetration of graphite layers inside the pores in thinner paper, but later it was excluded due to fragility. Thicker papers exhibited no significant conductivity variation ($p>0.05$, p value 0.4105), leading to the selection of 85GSM for further studies.

The number of deposited layers significantly impacts the overall conductivity of the electrode. The ohmic resistance progressively decreased with the incremental addition of layers, until reaching a threshold where further layering no longer contributed to conductivity improvements. For all paper thicknesses, the counter electrode and working electrode were optimized with two layers of graphite and modified CNTs as conductive ink, respectively, while the reference electrode required only one layer of silver paste. After the deposition of the initial layer, a sufficient absorption time was allowed to ensure proper penetration of the material into the electrode substrate before applying subsequent layers.

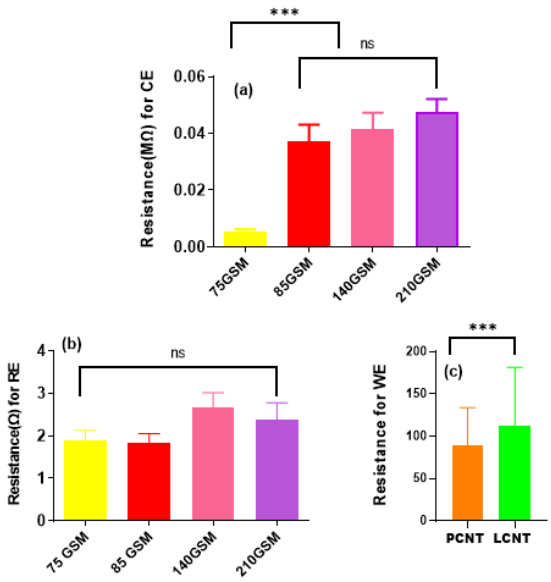

Figure 2: Resistance value across different thickness of office paper (75, 85, 140 and 210 GSM) (a) Resistance value for counter electrode (MΩ) (b) Resistance value for reference electrode (Ω) (c) Resistance value on 85GSM office paper for working electrode with different conductive ink [LCNT (kΩ) and PCNT(Ω)].

Optimization of Hydrophobic agent

To assess the impact of the hydrophobic barrier on the paper electrode, two sample electrodes were selected. In the first, wax crayon was applied, while in the second, the electrode was immersed in mineral oil until the hydrophobic region (demarcated by the orange line) was fully coated. The figure 3 clearly demonstrates that both methods are effective in confining the sample within the designated sample pad. So, a volatile organic free mineral oil shows to be effective in restricting the aqueous sample within the hydrophilic testing region. Mineral oil used stated its environment friendliness along with the ease of fabrication. For the wax deposition, the hydrophobic layer penetration was conducted through heating at a temperature of 121°C. Each paper type was optimized for heating on both sides for different durations according to its thickness factor, with the 75 GSM paper being treated for 5 minutes and the remaining types (85, 140, and 210 GSM) for 15 minutes

each. This variation in time could indicate that thinner papers require less time to absorb the wax, while thicker papers need extended heating to ensure complete integration of the hydrophobic barrier into the fibers.

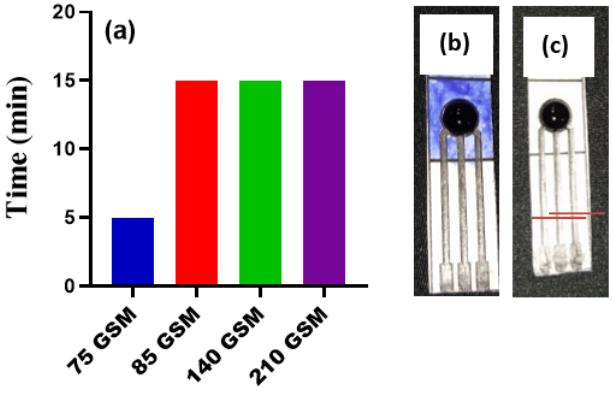

Figure 3: Optimized parameters (a) Time of heating required for different office paper for hydrophobic layer formation (b) Hydrophobic sample pad fabricated utilizing a wax-based crayon method (c) Hydrophobic sample pad fabricated utilizing a mineral oil method. Orange line indicated the mineral oil migration distance of 3.8 cm after immersion.

Electrochemical characterization of the fabricated electrodes

The paper electrodes were fabricated in two different dimensions along with two types of materials used for connections. The design aspect of electrode is an important factor for improving its efficiency. From the concept of electrochemistry and for the ease of fabrication an optimized design was selected through CV analysis as shown in figure 4. Here the two dimensions of electrode differing in certain aspects i.e. distance between reference and working electrode as well as counter surface area were compared. It was observed that an optimized design possessed lower current and selected for further study. Along with-it materials i.e. graphite and Ag paste were tested for connection where Ag always showed higher current compared to graphite but could cause overheating while working with biological buffers so graphite was used as optimized connection material.

To further evaluate the repeatability, reproducibility and lifetime of the electrodes the electrodes were evaluated for stability study through 25 cyclic scans on number of electrodes as shown in figure 5. The CV scans indicate the stability of the adsorbed materials on the engineered paper substrate, without any etching of the conductive ink. The electrochemical responses did not show any significant difference between number of electrodes scanned over a good period of time which showed its reproducibility along with a longer shelf life. This suggested that the platform is highly suitable for analytical feasibility related to biosensing and other electrochemical applications.

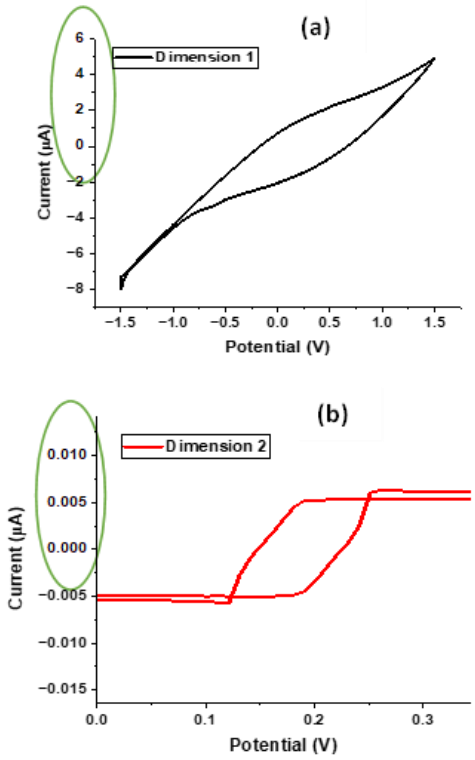

Figure 4: Electrochemical characterization of the electrode performed for (a) Dimension 1 (b) Dimension 2. The encircled region highlights a higher current response for Dimension 1 compared to Dimension 2.

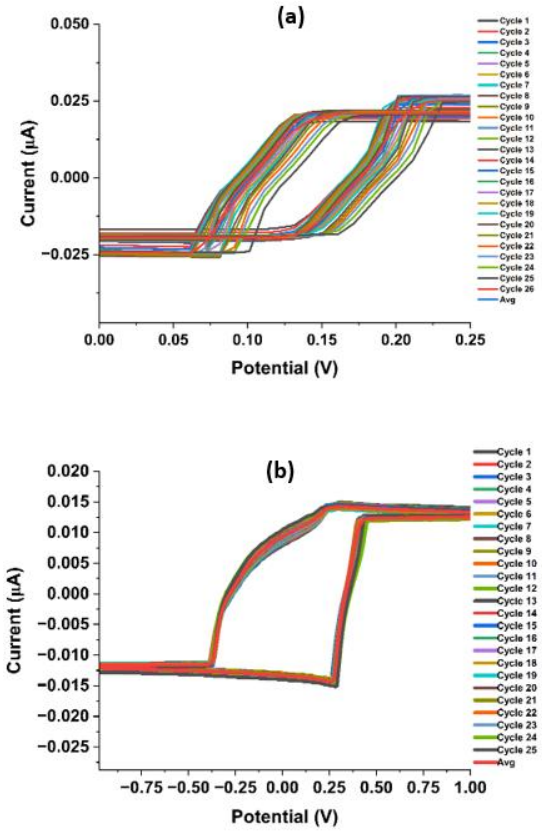

Figure 5: Stability of the conductive ink on 85 GSM, stability cycle (25 scans) for (a) LCNT on paper electrode (b) PCNT on paper electrode.

Conclusion and Future Prospective

The study had brought out optimization of different parameters to fabricate paper based electrochemical platform. The sustainability of the process to produce a final deliverable is the motivation and basis behind the work which is well achieved by using all environmentally friendly steps of fabrication. Two greener methods of modification of CNTs were successfully evaluated as conductive inks where PCNT showed 10 times higher conductivity to LCNTs attributing to its better ability of deagglomeration. The method of creating hydrophobic barrier was optimized with volatile-less oil and student wax crayon, additionally making the steps cost worthy and simple. The platform meets key REASSURED criteria, ensuring real-time connectivity (R) with a portable potentiostat, efficient sample collection (E) using 50 µL of non-invasive fluids, affordability (A) with cost-effective materials, user-friendliness (U), rapid analysis (R), and robustness, as the electrodes are disposable and recyclable. The selectivity and sensitivity (SS) of the paper platform for dopamine sensing with further improvisation in design will be investigated in the future work. The overall material selection had resulted in stable electrochemical response of the platforms showing its promising application not only in biosensing but also in varied other electrochemical processes.

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