Trends in Analytical Chemistry 204 (2026) 119024

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Paper-based electrochemical (bio)sensors as advanced and sustainable wearable devices

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ARTICLE INFO

Keywords:
Point-of-care devices
Precision agriculture
Real-time environmental monitoring
Sweat
Breath

ABSTRACT

Wearable electrochemical (bio)sensors have emerged over the last few decades as versatile analytical platforms for decentralized healthcare. Cellulose-based substrates are characterized by intrinsic properties, including porosity, foldability, breathability, and mechanical robustness, which can be exploited to enable advanced wearable devices.

This review critically examines how the features of the paper have enabled reagent-free designs, origami-inspired architectures, humidity-driven activation mechanisms, and modular strategies for electronic integration in advanced wearable electrochemical devices. Furthermore, it surveys recent applications in sweat and breath analysis, wound monitoring, plant diagnostics, and environmental surveillance, highlighting the key role of paper-based wearable electrochemical (bio)sensors as a future direction for the development of smart and sustainable wearable analysis.

1. Introduction

According to the World Economic Forum forecasts, the paradigm of disease diagnosis is expected to undergo a profound transformation by 2030, driven by rapid technological innovation [1]. The so-called Fourth Industrial Revolution is expected to extend average lifespan and improve the quality of life through the integration of digitalization, advanced sensing technologies, artificial intelligence, and interconnected healthcare systems. Within this framework, healthcare models are progressively shifting from centralized hospital-based systems toward decentralized data-driven paradigms. Hospitals are expected to evolve into facilities primarily dedicated to acute and highly specialized interventions, while routine monitoring and early diagnosis will increasingly occur outside traditional clinical settings, marking the transition from hospital-centered care to distributed "home-spital" models.

Wearable electrochemical (bio)sensors are well-positioned within this evolving scenario as a transformative technology enabling the transition from centralized diagnostics to decentralized healthcare. Electrochemical transduction represents a relevant key approach due to its intrinsic sensitivity, robustness, compatibility with continuous monitoring, low power consumption, ease of miniaturization, scalability in manufacturing, and high compatibility with flexible and soft substrates.

The pioneering contributions of Joseph Wang established the feasibility of wearable electrochemical platforms for real-time analysis of several target analytes in sweat, saliva, tears, and other biofluids, implemented in diverse configurations, including rings, pacifiers, gloves, and robotic systems [2–5]. These studies demonstrated that electrochemical biosensors provide dynamic molecular-level information using a wearable configuration. Wei Gao's research group is further expanding the application of wearable electrochemical biosensing with advanced configurations harnessing flexible electronics for unprecedented applications [6–8], for instance, by developing an autonomous wearable device powered by a perovskite solar cell [9] or by monitoring female reproductive hormones in real-world settings [10,11].

The foundational advances have facilitated the translation of wearable electrochemical biosensing into clinically validated commercial systems. Continuous glucose monitoring devices such as FreeStyle Libre (Abbott Laboratories) [12] and Dexcom G6 (Dexcom) [13] represent milestone examples of the successful integration of minimally invasive electrochemical biosensing tools, miniaturized electronics, and digital health infrastructures. These systems clearly demonstrate the translational potential of electrochemical biosensors, achieving regulatory approval, scalable production, and broad clinical implementation, thereby improving the quality of life of patients with diabetes and

This article is part of a special issue entitled: POCT devices published in Trends in Analytical Chemistry.

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https://doi.org/10.1016/j.trac.2026.119024
Received 18 March 2026; Received in revised form 14 June 2026; Accepted 8 July 2026
Available online 8 July 2026
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reducing the economic burden on healthcare systems.

Recently, wearable electrochemical (bio)sensors have expanded beyond traditional biomedical applications into breath analysis and the agri-food domain, broadening their technological and societal impact [14–18]. The adaptation of wearable sensing concepts to exhaled breath has permitted non-invasive platforms capable of detecting volatile organic compounds and disease-related biomarkers, opening new avenues for early diagnosis and real-time health assessment. In parallel, the translation of flexible and wireless biosensing technologies into plant systems has boosted plant wearable (bio)sensors to directly monitor physiological stress and nutrient status. The growing importance of these technologies has also been recognised by the World Economic Forum, which included breath sensors for disease diagnosis among the Top 10 Emerging Technologies of 2021 [19] and wearable plant sensors among the Top 10 Emerging Technologies of 2023 [20].

Within this evolving landscape and considering the increasing emphasis on sustainability, electrochemical paper-based (bio)sensors have emerged as a new generation of sustainable analytical devices, recently influencing the wearable sector. Paper substrates possess unique properties, including intrinsic capillarity, high surface-to-volume ratio, mechanical flexibility, low cost, and biodegradability. These characteristics position paper-based devices not only as ecodesigned analytical tools but also as platforms with distinctive functional advantages: self-driven microfluidics without external pumps, mitigation of bubble-related issues common in polymer-based systems, smooth integration of electrodes and sampling zones, reagent-free operation through dried reagent storage within the cellulose network, and compact, disposable architectures [21–25].

To date, to the best of my knowledge, only one dedicated mini-review has specifically addressed paper-based wearable electrochemical sensors [26], focusing primarily on paper as a smart substrate, wearable technology from sampling to the Internet of Things (IoT), and multiplexing strategies. However, several recent advances have considerably expanded the field and highlighted new opportunities that remain insufficiently discussed from a material-centric perspective. In particular, the active role of paper in enabling passive fluid handling, reagent compartmentalization, simplified microfluidic architectures, origami-inspired designs, humidity-driven activation mechanisms, and seamless integration with flexible and wireless electronics.

Accordingly, this review adopts a different conceptual framework by considering paper not merely as a passive support but as an active structural and functional material that directly governs sampling, analyte transport, sensing mechanisms, and device architecture. Furthermore, beyond conventional sweat and wound monitoring, the review discusses emerging applications including breath analysis, plant diagnostics, and environmental surveillance, thereby providing an updated and broader perspective on the design and future development of wearable paper-based electrochemical (bio)sensors (Fig. 1).

2. Paper features for smart wearable electrochemical (bio) sensors

2.1. Porosity of the paper for capillarity-driven devices

One of the key advantages of wearable paper-based electrochemical (bio)sensors lies in their porosity–capillarity-driven operation, which enables autonomous fluid handling without the need for external pumping systems. The interconnected cellulose fiber network generates intrinsic capillary forces that promote spontaneous sample uptake, transport, and distribution across the sensing interface. This self-driven microfluidic behaviour simplifies device architecture, reduces energy requirements, and enhances robustness, avoiding the bubble issues, features that are particularly critical in wearable configurations, where mechanical simplicity and low power consumption are essential. The high surface-to-volume ratio provided by the porous cellulose matrix further facilitates rapid analyte diffusion and efficient interaction with functionalized electrodes. As a result, capillarity is not merely a passive transport mechanism, but a fundamental design principle governing response time, sensitivity, and fluid renewal at the electrode interface. The exploitation of porosity for capillarity-driven devices represents a key enabler for lightweight, disposable, and fully integrated wearable analytical systems.

A particularly relevant example was reported by the Velev group, who developed a wearable system for real-time lactate detection in sweat, integrating an osmotic hydrogel layer to induce and collect perspiration, a paper-based microfluidic pathway ensuring controlled fluid handling, and a printed lactate biosensor [27]. In detail, they designed the paper-based microfluidic pathway encompassing i) a circular sampling region with two side incisions to minimize the area that must be wetted, thereby rapidly saturating the sensing region, ii) a serpentine configuration to increase the effective surface area between the circular inlet and the evaporation compartment by roughly 90%, and iii) the evaporation reservoir to increase the evaporation rate ensuring a continuous renewal of fresh sweat over the sensing electrodes. This configuration allowed the detection of lactate with a linear response up to 10 mM and a sensitivity of 172 nA $mM^{-1}mm^{-2}$.

Fiore et al. engineered a cellulose microfluidic architecture to empower controlled lateral capillary flow and ensure continuous sweat renewal at the electrode surface in a new wearable electrochemical device based on butterfly-like paper microfluidics for pH and Na^+ monitoring in sweat [28]. In detail, the cellulose-based microfluidic system was produced with a CO_2 laser cutter and commercial absorbent paper (Scottex®), yielding a structure resembling a butterfly (Fig. 2A). The two symmetrical extensions of this layout were engineered to

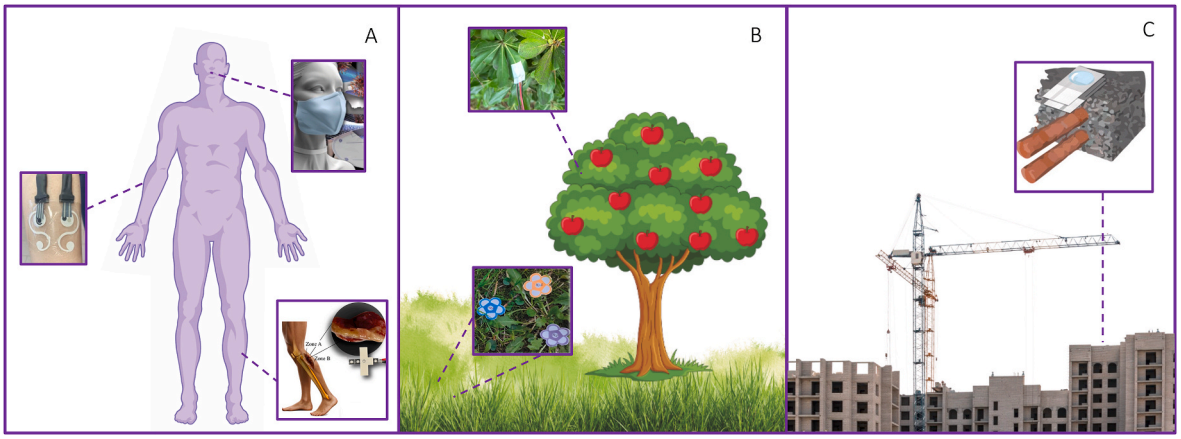


Fig. 1. Paper-based electrochemical wearable (bio)sensors for applications in biomedical diagnostics (A), agri-food monitoring (B), and environmental analyses (C).

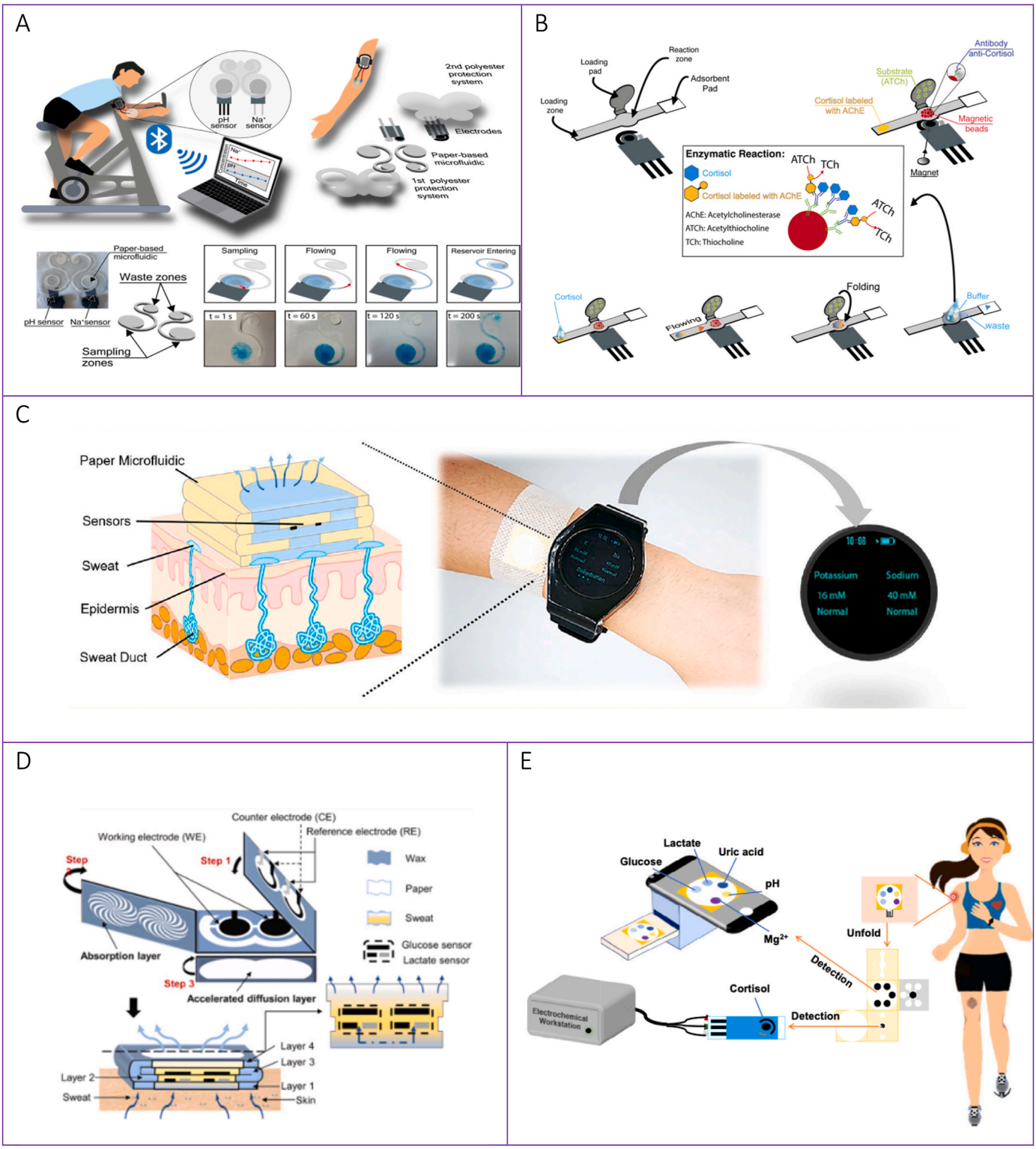


Fig. 2. Harnessing i) paper porosity for capillary-driven and reagent-free wearable paper-based electrochemical (bio)sensors and ii) foldability for origami paper-based wearable electrochemical (bio)sensors. A) Paper-based butterfly-like microfluidics integrated with pH and Na^+ potentiometric sensors for real-time monitoring of pH and Na^+ in sweat. Reproduced with permission [28]. B) Reagent-free paper-based electrochemical immunosensor based on the use of paper-based microfluidics and magnetic beads for one-spot analysis of cortisol in sweat. Reproduced with permission [31]. Origami paper-based microfluidics combined with potentiometric sensors for Na^+ and K^+ detection in sweat C) [34] or with amperometric biosensors for glucose and lactate in sweat D) [35]. Reproduced with permission [34,35]. D) Origami paper-based device for multiple detection of glucose, lactate, uric acid, pH, and cortisol. Reproduced with permission [36].

interface separately with the pH-selective and Na^+-selective potentiometric electrodes. The working mechanism of the platform is based on the coexistence of two distinct functional domains: collection regions and drainage regions. The collection regions are responsible for harvesting freshly secreted perspiration and simultaneously constitute the sensor interface, as they are directly coupled to the sensing electrodes for potentiometric readout. Following detection, the fluid is spontaneously transported toward the drainage regions through a 2 mm-wide linking microchannel. In these regions, an absorbent pad captures and retains the liquid sample. This component performs a dual function, operating as a capillary-driven passive pumping element and as a reservoir for excess fluid. The geometry of both the collection and drainage sections, along with the interconnecting microchannel, was refined by monitoring liquid propagation across one side of the butterfly-shaped structure. This design permitted continuous uptake of newly generated sweat with accurate real-time monitoring of the target species. Notably, liquid movement within the device is governed solely by capillary action rather than evaporation-based transport mechanisms. Importantly, hysteresis studies performed under increasing and decreasing analyte concentrations demonstrated negligible memory effects. The absence of signal hysteresis confirmed that capillarity-driven fluid replacement effectively prevents analyte accumulation and carryover within the porous network. The sensitivities obtained, equal to (-0.084 ± 0.004) V/pH and (0.061 ± 0.002) V/dec for pH and Na^+, respectively, together with the successful analyses performed during a standardized cardiopulmonary exercise test on a medical stationary bicycle, clearly demonstrated that properly designed paper-based microfluidics can facilitate true continuous monitoring under dynamic physiological conditions, allowing for real-time analysis of sweat biomarkers.

In this vein, the porosity-driven architectures provide the structural basis for reliable continuous monitoring by governing fluid renewal, minimizing memory effects, and ensuring stable analyte–electrode interaction under dynamic physiological conditions. However, different capillarity-driven strategies exhibit distinct trade-offs. Systems relying on evaporation-assisted flow enable continuous sample renewal but may be influenced by ambient temperature and humidity, potentially affecting sampling reproducibility under real-world conditions. In contrast, architectures based exclusively on capillary-driven transport reduce dependence on environmental factors and effectively minimize hysteresis, although they require careful optimization of channel geometry and absorbent reservoirs to maintain sustained flow over prolonged operation. More generally, the successful implementation of passive microfluidics depends not only on the intrinsic porosity of paper but also on the rational engineering of fluidic pathways to balance sampling efficiency, response stability, manufacturability, and user comfort. Consequently, capillarity should be regarded not merely as a transport mechanism but as a key design parameter governing the analytical reliability and translational potential of wearable paper-based electrochemical (bio)sensors.

2.2. Porosity of the paper for reagent-free devices

The fabrication of reagent-free analytical tools is a highly attractive goal in the field of electrochemical sensing and is almost mandatory for wearable devices, where operational simplicity, user independence, and portability are essential. In wearable configurations, the end user should ideally wear the device without performing additional steps, such as reagent addition, pH adjustment, or solution preparation. In this regard, the intrinsic porosity of cellulose substrates offers a decisive advantage. The fibrous structure of filter paper provides a high loading capacity and enables immobilization of chemical reagents directly within the porous matrix. Reagents can be preloaded in dry form and subsequently released upon capillary-driven hydration by the sample, thereby transforming the paper substrate into a multifunctional scaffold that integrates reagent storage, sampling, reaction, and electrochemical transduction within a single material platform [29].

A representative example is provided by Parrilla et al. [30], who exploited the loading capability of Whatman grade 1 filter paper to pre-store the acidic solution required for phenylalanine detection in saliva and serum using a wearable analytical tool. In this configuration, the paper substrate simultaneously facilitated sample collection and reagent release upon hydration, simplifying the analytical workflow while maintaining a compact device architecture. The integration of reagent storage within the cellulose network eliminated the need for external reagent handling, obtaining a calibration curve with a slope of 0.043 $\mu A\ \mu M^{-1}$ in saliva and representing a step toward reagent-free devices. Beyond simple reagent preloading, cellulose porosity enables the spatial compartmentalization of multiple assay components. This design strategy is particularly relevant in wearable immunosensors, where biochemical complexity must be translated into operational simplicity. A paradigmatic example is the wearable paper-based microfluidic device developed for cortisol monitoring in sweat based on a competitive magnetic-bead immunoassay [31]. In this system, the cellulose substrate was engineered to host distinct functional zones, each assigned a specific role. The enzyme-labeled cortisol conjugate (cortisol–acetylcholinesterase) and the enzymatic substrate (acetylthiocholine) were preloaded and physically entrapped within defined regions of the paper matrix, namely the loading zone and the loading pad, respectively (Fig. 2B). The high absorption capacity and retention properties of cellulose fibers ensured stable dry storage of these reagents, which were subsequently activated upon capillary-driven hydration by sweat. In contrast, magnetic beads functionalized with capture antibodies were confined within the reaction zone using an external magnet. This magnetic confinement strategy ensured precise localization of the immunocomplex at the electrode interface, minimizing dispersion of antibody-functionalized beads within the porous network and enhancing assay reproducibility. The sensing mechanism relied on a competitive interaction between endogenous cortisol and the preloaded enzyme-tagged cortisol. Upon folding the substrate-containing pad into contact with the reaction zone, the enzymatic reaction was triggered, generating an electrochemical signal inversely proportional to cortisol concentration, with a linear range of 10-140 ng/mL. The spatial separation of assay components namely the enzyme-labeled cortisol and the enzymatic substrate embedded within the cellulose matrix, and antibody-functionalized magnetic beads magnetically controlled at the sensing interface, demonstrates how cellulose porosity can be engineered to support reagent immobilization, controlled activation, and localized reaction kinetics. This compartmentalization strategy significantly reduces procedural steps, eliminates user-dependent reagent manipulation, and moves wearable electrochemical platforms closer to fully autonomous dry-chemistry systems. Within this framework, cellulose porosity emerges not merely as a passive reagent reservoir, but as a structural material that allows spatial organization, controlled activation, and simplification of complex bioassays. By integrating reagent storage and electrochemical transduction within a single porous network, paper-based architectures reduce user intervention while preserving analytical performances. Nevertheless, implementing reagent-free strategies also could pose significant challenges. The long-term stability of preloaded reagents may be affected by environmental factors such as humidity, temperature, and oxidation during storage, potentially compromising assay reproducibility and shelf life. In this regard, appropriate packaging solutions, including vacuum sealing or storage in moisture-barrier pouches with desiccants, may be required to preserve reagent activity over extended periods. Although compartmentalization strategies effectively simplify user operation and reduce procedural steps, they may increase fabrication complexity and require careful optimization of reagent localization. However, the successful large-scale manufacturing of colorimetric lateral flow assays demonstrates that industrial implementation of reagent preloading and spatial compartmentalization is technically feasible, providing a valuable benchmark for the future

commercialization of paper-based wearable electrochemical (bio)sensors. Therefore, the rational engineering of reagent compartmentalization within cellulose substrates represents not only a decisive step toward fully autonomous wearable electrochemical systems but also an opportunity to leverage established manufacturing concepts to achieve robust, scalable, and commercially viable dry-chemistry platforms.

2.3. Foldability of the paper for origami configuration

Beyond porosity, the intrinsic foldability of paper offers a distinctive structural advantage for the development of wearable electrochemical (bio)sensors. The mechanical flexibility of cellulose substrates allows for the transformation of two-dimensional patterned devices into three-dimensional architectures through simple folding. In this context, origami-inspired design is not merely a geometric rearrangement, but a functional strategy that enables spatial separation and programmable interaction of sampling zones, reagent reservoirs, reaction chambers, and detection electrodes within a single planar substrate [32,33].

In wearable systems, foldability becomes an active design principle governing device functionality and analytical workflow. By folding predefined layers into contact, fluidic pathways can be activated, reagents can be brought into controlled interaction, and electrochemical cells can be assembled only at the time of measurement. This temporal and spatial control is particularly advantageous for multiplexed analyses. Cao et al. [34] developed a smartwatch integrated with a paper-based microfluidic patch for monitoring sodium and potassium ions in sweat at the millimolar level. In this system, the engineered paper-based patch integrated a dedicated sweat collection module and a flow-cell architecture designed to regulate fluid transport and evaporation within the device (Fig. 2C). This configuration facilitated controlled sweat uptake and directional flow while limiting the intermixing of previously accumulated and newly secreted sweat during the analytical process. The reduced mixing effect was attributed to predominantly diffusive, convection-free ion transport within the liquid-filled porous paper channels. The paper-based platform was tested during constant-load cycling exercise, with ion measurements recorded at 1 min intervals. Potassium levels in sweat remained stable (ca. 4 mM) during prolonged exercise, consistent with passive partitioning and minimal dependence on sweat rate, likely reflecting muscle fatigue–related dynamics. Sodium concentrations fluctuated within 40–80 mM or 60–80 mM in different subjects without sharp increases, indicating modulation by sweat rate rather than dehydration and suggesting effective physiological regulation. Consistent pre- and post-test calibration responses confirmed sensor stability, supporting the reliability of the wearable ion-selective platform for real-time correlation between sweat ion profiles and physiological status.

Similarly, Li et al. [35] developed a highly integrated paper-based biosensing platform for wearable electrochemical analysis of glucose and lactate in sweat, exploiting multilayer cellulose architectures to combine microfluidic transport and electrochemical detection within a single compact platform (Fig. 2D). The vertical stacking of paper layers enabled controlled sweat delivery to multiple sensing zones while maintaining mechanical compliance suitable for on-body applications, allowing for the simultaneous detection of glucose and lactate with a sensitivity of 2.4 nA μM^{-1} and 490 nA mM^{-1}, respectively.

More recently, Cheng et al. [36] reported a wearable biosensor based on a three-dimensional origami structure combining dual-signal readout (optical and electrochemical) (Fig. 2E). This configuration enhanced analytical compartmentalization, illustrating how origami architectures can expand the functional complexity of wearable paper-based systems without increasing fabrication burden. Beyond previous research, this research used a molecularly imprinted polymer (MIP) as a sensing material for the detection of the target analyte cortisol. This sensing mechanism is based on the principle that different concentrations of cortisol molecules occupy the MIP cavity, hindering the charge transfer in Prussian blue, yielding a calibration curve between 10^{-9} to 10^{-6} M. However, while vertical paper-based microfluidics, where the sample is added from the top and transported downward, allows for more precise control of the introduced volume and the flow rate through the combined effects of capillarity and gravity, wearable sweat-sampling configurations often operate under different conditions. In many epidermal origami devices, sweat is absorbed from the skin-facing bottom layer and transported upward through the cellulose network. This bottom-to-top microfluidic pathway reduces control over the effective sampled volume, as flow dynamics become strongly influenced by time- and temperature-dependent evaporation. Evaporation within the porous cellulose layers can induce analyte preconcentration, a phenomenon previously reported in paper-based systems. While preconcentration may increase signal intensity, in the context of sweat analysis it can lead to overestimation of the analyte concentration, particularly during prolonged wear or under elevated environmental temperatures. Therefore, although origami-based configurations offer clear advantages in integration, miniaturization, and multiplexing, careful engineering of the microfluidic pathway and evaporation management is essential to ensure accurate data.

2.4. Mechanical flexibility of the paper for well-comfortable wearable devices

Mechanical flexibility is a key requirement for wearable paper-based electrochemical (bio)sensors, as these devices must conform to curved and dynamically moving surfaces without compromising analytical performance. The intrinsic compliance of cellulose substrates, arising from their fibrous porous architecture, enables bending and twisting while preserving structural integrity and electrode functionality. This mechanical adaptability reduces motion-induced artefacts, maintains stable biofluid–electrode contact, and enhances user comfort during prolonged wear.

A representative example is the integrated paper-based patch developed for the non-invasive detection of diabetic nephropathy biomarkers namely glucose, creatinine, and uric acid in sweat [37]. To preserve both conductivity and flexibility, all electrodes were modified using acrylamide-doped PEDOT:PSS conductive ink. This modification imparted high electrical conductivity while maintaining the porous structure of the paper substrate, thereby maximizing the electrochemically active surface area without compromising mechanical compliance. The preservation of porosity ensured efficient sweat transport, while the conductive polymer layer provided stable electrochemical performance under mechanical stress. Importantly, the mechanical robustness of the integrated paper-based patch was systematically evaluated. After 1000 bending cycles at 90°, the device exhibited less than 5% signal variation, demonstrating excellent stability under repeated deformation (Fig. 3A). This quantitative evidence confirms that properly engineered cellulose-based platforms can withstand mechanical stress typical of real-world wearable conditions without significant analytical degradation. This disposable platform, combining a capillary-driven microfluidic module, iontophoresis electrodes for on-demand sweat stimulation, and a multi-analyte electrochemical sensor array, demonstrated strong agreement between this wearable platform and reference methods (HPLC and commercial colorimetric kits) in on-body testing, with correlation coefficients of 0.98, 0.96, and 0.93 for glucose, creatinine, and uric acid, respectively.

Overall, mechanical flexibility in paper-based wearable electrochemical systems is not merely a comfort-related feature but a determinant of signal stability, reproducibility, and long-term reliability. However, increasing mechanical compliance may also introduce challenges that deserve careful consideration. Repeated bending, twisting, or stretching can promote microcrack formation, delamination of printed conductive layers, or changes at the electrode/substrate interface, potentially affecting long-term signal stability and reproducibility. In addition, excessive deformation may alter the porous network geometry and affect capillary-driven fluid transport. Although conductive polymer

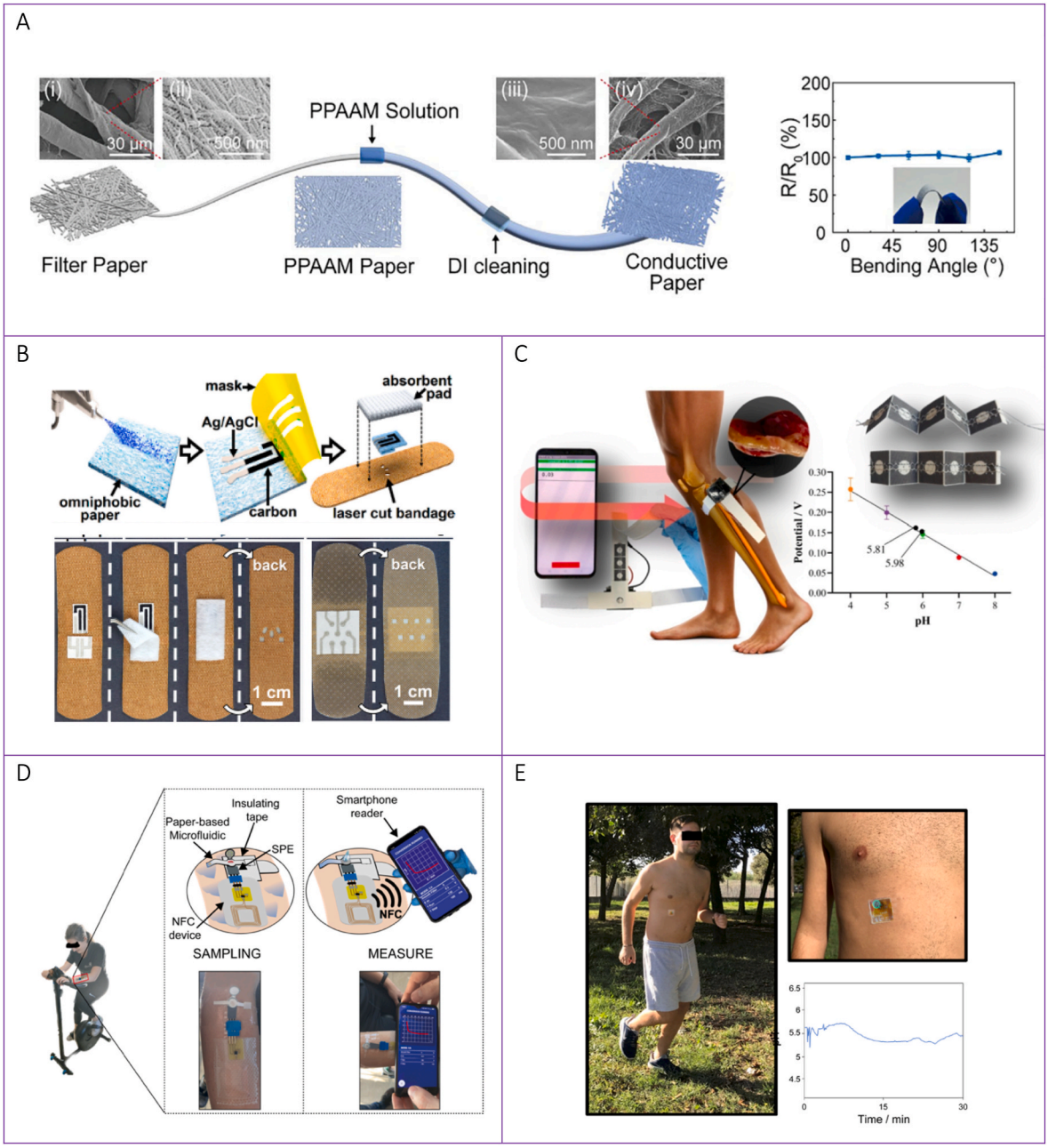


Fig. 3. Paper-based wearable electrochemical (bio)sensors i) characterized by mechanical flexibility, breathability, and ii) integrated with other technologies, including embroidery, NCF, and RFID. A) Paper-based wearable electrochemical (bio)sensors based on acrylamide-doped PEDOT:PSS conductive ink with mechanical robustness testing with 1000 bending cycles at 90°. Reproduced with permission [37]. B) Omniphobic paper-based smart bandages characterised by breathability for the detection of pH and uric acid in wounds. Reproduced with permission [38]. C) Embroidered wearable paper-based electrochemical device for pH detection in wounds. Reproduced with permission [41]. D) NFC-based electrochemical immunosensor for cortisol detection in sweat. Reproduced with permission [31]. E) RFID-based potentiometric sensor for pH monitoring in sweat. Reproduced with permission [43].

coatings and optimized device architectures effectively mitigate these issues, the studies related to bending, twisting, and stretching are required for any developed device to evaluate durability during prolonged wear. Therefore, the design of mechanically flexible paper-based wearable electrochemical (bio)sensors should balance user comfort with structural robustness to ensure reliable analytical performances and facilitate translation toward practical and commercial applications.

2.5. *Breathability of the paper for accurate on-skin analysis*

Breathability is a crucial yet often underestimated parameter in the design of wearable paper-based electrochemical (bio)sensors. Unlike polymeric or fully encapsulated flexible substrates, cellulose-based materials inherently exhibit high air and vapor permeability owing to their interconnected fibrous network. This intrinsic characteristic enhances skin compatibility during prolonged wear by facilitating heat dissipation and preventing excessive moisture accumulation at the skin–device interface, a feature particularly relevant for continuous monitoring applications. However, breathability is not solely a comfort-related property. From an analytical point of view, vapor permeability influences fluid dynamics and signal reproducibility. A representative example is the low-cost omniphobic paper-based smart bandage for early detection and monitoring of chronic wounds reported by Pal et al. [38]. In this work, the paper substrate was engineered to combine

electrochemical sensing with vapor permeability and controlled interaction with wound exudate (Fig. 3B). The breathable architecture allowed gas exchange at the wound interface while supporting real-time electrochemical monitoring of pH and uric acid in the ranges of 5–9 and 0.2–1 mM, respectively. Importantly, the omniphobic surface treatment regulated liquid penetration, preventing uncontrolled fluid spreading while preserving vapor diffusion. This balanced design demonstrated how cellulose can be engineered to simultaneously ensure breathability, fluid control, and analytical functionality in skin-interfaced devices. Additional evidence highlighting the importance of breathability has been reported in flexible wearable sensing systems employing breathable encapsulation layers. In these devices, efficient vapor permeability enabled the diffusion of volatile analytes, producing a detectable pH change within 1 s, thereby confirming rapid gas exchange through the protective layer [39]. Moreover, prolonged on-body tests demonstrated excellent skin compatibility: after 7 days of continuous wear, no visible inflammation or allergic reactions were observed beneath the paper-based breathable sensor, whereas conventional polyurethane (PU) films and commercial adhesive bandages induced noticeable skin irritation [40]. These findings quantitatively demonstrate that optimized breathability not only enhances wearer comfort but also minimizes sweat accumulation and skin occlusion compared with traditional polymeric materials, supporting more stable long-term operation under realistic conditions.

Overall, breathability should be regarded as a strategic design parameter in wearable paper-based electrochemical (bio)sensors rather than as a secondary material attribute. Beyond improving comfort, appropriate vapor exchange can enhance signal stability by limiting moisture accumulation at the skin–sensor interface while preserving the functionality of sensing components during prolonged use. However, excessive evaporation may lead to analyte preconcentration or reagent drying, indicating that the balance between breathability and fluid retention must be carefully optimized. The intentional tuning of air permeability, surface wettability, and evaporation dynamics therefore becomes essential for ensuring reliable, long-term, and robust on-body monitoring.

3. Paper as a collaborative material

3.1. Compatibility with different fabrication technologies

A distinctive strength of wearable paper-based electrochemical (bio) sensors is their compatibility with a wide range of fabrication technologies. Cellulose substrates are inherently suited for additive manufacturing approaches due to their thermal stability under moderate curing conditions, surface roughness favorable to ink adhesion, and mechanical compliance. This compatibility enables the integration of electrochemical transducers, microfluidic patterns, and structural components within scalable and cost-effective production workflows. Beyond conventional screen-printing of conductive inks, paper substrates can be integrated into textile manufacturing processes, aiding hybrid paper–fabric analytical systems. A pioneering example is the electrochemical microfluidic thread/paper-based analytical device, representing the first demonstration of combining embroidery with paper-based electrochemical microfluidics [41]. In this configuration, conductive silver threads coated with graphite and Ag/AgCl inks were embroidered onto filter paper to form the working and reference electrodes, respectively (Fig. 3C). The working electrode was further modified by electrodeposition of an iridium oxide film for potentiometric pH sensing. The embroidered threads, embedded within the cellulose substrate, created a flexible electrochemical cell integrated into a paper microfluidic architecture. This hybrid configuration enabled wearable pH monitoring in chronic wounds over the physiological range of pH 4–8, with a sensitivity of 0.056 ± 0.002 V/pH and a reproducibility of 8%. Importantly, the modular design allowed for renewal of the sensing pad by simply cutting and replacing the μthread–paper unit after use, enhancing practicality in wound-monitoring scenarios. This work demonstrated that embroidery, which is a mature and scalable textile technique, can be successfully merged with paper-based electrochemical sensing, expanding fabrication strategies beyond planar electrode printing.

Another example of the convergence of additive manufacturing techniques isparticular promise for early disease detection and reported by Iula et al. [42], who developed an on-body electrochemical lactate biosensor integrating screen-printed electrodes, paper-based fluidics, and a 3D-printed thermoplastic polyurethane armband. The 3D-printed TPU support provided ergonomic customization, mechanical stability, and structural integration with a screen-printed electrode modified with Prussian blue/carbon black/lactate oxidase and a filter paper strip for sweat collection and transport, allowing for the detection of lactate with a detection limit of 60 μM and a linearity up to 20 mM.

These examples, together with those discussed in the previous sections, which employed techniques such as wax printing or laser cutting to fabricate microfluidic structures, highlight how paper can be effectively combined with diverse technologies suitable for mass production.

3.2. Synergy with wireless integration strategies

The evolution of wearable paper-based electrochemical (bio)sensors toward fully functional analytical tools is strongly driven by advances in flexible and printed electronics. While cellulose substrates provide passive microfluidics, reagent compartmentalization, mechanical robustness, and sustainability, the electronic components govern signal conditioning, data processing, power management, and wireless communication. Therefore, the technological maturity of wearable paper-based devices lies not only in electrochemical sensing, but also in the system-level integration between disposable paper-based analytical interfaces and reusable electronic modules.

Recent developments highlight three principal wireless integration strategies, namely ultra-high-frequency (UHF) radio-frequency identification (RFID), near-field communication (NFC), and Bluetooth Low Energy (BLE), each addressing different operational scenarios. From an electronic standpoint, UHF-RFID architectures enable medium-distance interrogation through passive or semi-passive backscattering mechanisms, minimizing on-board energy requirements while allowing remote data retrieval. NFC-based systems operate via inductive coupling at short range, enabling ultra-low-power or battery-free configurations with direct smartphone compatibility. BLE modules, in contrast, provide continuous bidirectional communication and real-time data streaming, supporting dynamic physiological monitoring but requiring more structured power management and circuit integration.

Although all three technologies can be successfully integrated into paper-based wearable electrochemical (bio)sensors, they differ substantially in operating distance, data rate, power consumption, battery requirements, and smartphone compatibility, making each strategy suitable for specific applications. A comparison of their main technical characteristics, typical use in paper-based wearable systems, and advantages and disadvantages are provided in Table 1 to aid in selecting the most appropriate wireless platform for the selected application. In detail, while the previous examples mainly employed NFC (Fig. 3D) and BLE systems, Mazzaracchio et al. [43] reported the first UHF-RFID paper-based platform. The authors developed a wireless and flexible epidermal device for pH monitoring in sweat, integrating a screen-printed potentiometric sensor, an integrated circuit, and an antenna onto the same Kapton substrate with a cotton-derived sampler (Fig. 3E). The sensing architecture was fabricated through screen-printing of both the electronic circuitry and the electrochemical components onto the same Kapton substrate, resulting in a monolithic and fully printed patch. pH detection in sweat was achieved using iridium oxide as the pH-responsive layer, while sweat collection and delivery to the sensing interface were ensured through a cotton-derived element acting as a paper-based microfluidic pathway. Wireless

Table 1
Comparison of the main wireless communication technologies used in paper-based wearable electrochemical (bio)sensors.

Technology	Operating distance	Data rate	Power consumption	Battery requirement	Smartphone compatibility	Typical use cases in paper-based wearable systems	Advantages/Disadvantages
BLE	10–100 m	e.g. 1.3 Mbps[a]	Low	Yes	Excellent	glucose and/or lactate [27,35,44], pH and sodium [28], glucose, creatinine, and uric acid [37].	Continuous wireless transmission and real-time communication with smartphones/Increased energy consumption and circuit complexity
NFC	<10 cm (typically 2–5 cm)	e.g. 424 kbps[b]	Very low (passive)	No	Excellent	cortisol [31]	Battery-free operation and direct smartphone interfacing/Very short communication range
UHF-RFID	1–10 m	e.g. 55.5 kbps[c]	Very low (passive or semi-passive)	No (passive), yes (semi-passive)	Limited (external reader often required)	pH [43]	Longer interrogation distance with passive operation/Requires dedicated RFID infrastructure

[a] R. Katila, T.N. Gia, T. Westerlund. Analysis of mobility support approaches for edge-based IoT systems using high data rate Bluetooth Low Energy 5. Computer Networks 209 (2022) 108925. https://doi.org/10.1016/j.comnet.2022.108925.
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communication was implemented using a UHF-RFID system, providing a substantially longer interrogation distance than NFC and improved power management compared to BLE, including the possibility of fully battery-free real-time operation. The device exhibited a near-Nernstian response of -0.079 ± 0.002 V per pH unit in buffer solutions. The integrated epidermal platform was evaluated for real-time monitoring during running activity, showing sweat pH values around 5.5, in agreement with measurements obtained using a conventional pH meter as reference, thereby demonstrating the reliability of the wearable system.

This example clearly shows that, beyond communication protocols, printed and flexible electronics play a critical role in signal acquisition and processing. However, the separation between the sustainable analytical interface and the durable electronic core represents a key strategy to reduce electronic waste while preserving analytical functionality. Furthermore, power management strategies, such as low-power communication protocols, thin-film batteries, and energy-harvesting modules, need to be considered for wearable applications. Mechanical design considerations are equally critical. Flexible interconnects and selective encapsulation layers mitigate the mechanical mismatch between rigid microelectronic components and compliant cellulose substrates. From this perspective, wearable paper-based electrochemical (bio)sensors should not be regarded as isolated analytical patches, but as interconnected analytical nodes within distributed digital ecosystems.

4. Paper-based wearable electrochemical (bio)sensors for unprecedented applications

4.1. Biomedical field

Throughout the previous sections, wearable electrochemical (bio) sensors for sweat and wound exudate analysis have been discussed as representative examples to illustrate how the intrinsic properties of paper govern device architecture, fluid management, and analytical performance. Building on these concepts, this section focuses on breath analysis as an emerging biomedical application and demonstrates the versatility of paper-based wearable electrochemical (bio)sensors across different biological matrices.

Exhaled breath contains a complex mixture of volatile organic compounds (VOCs), inorganic gases, and aerosolized biomarkers that can reflect metabolic status, inflammatory processes, and disease progression. Breath analysis offers a completely non-invasive alternative to blood sampling, with particular promise for early disease detection and real-time physiological monitoring [45]. In this context, paper-based electrochemical platforms provide unique material and functional advantages. The intrinsic porosity and high surface-to-volume ratio of cellulose substrates facilitate rapid diffusion of gaseous analytes toward functionalized sensing interfaces. Unlike dense polymeric materials, paper allows efficient gas permeability, facilitating direct interaction between volatile species and catalytic or enzymatic layers deposited onto printed electrodes [15,46]. A pioneering example of breath analysis using a paper-based electrochemical platform was reported by Dincer and co-workers in 2019 [47]. They developed an electrochemical paper-based analytical device printed with Prussian Blue-modified ink for hydrogen peroxide quantification in simulated breath with a sensitivity of 0.19 nA μM^{-1} mm^{-2} (Fig. 4A). In this system, the paper substrate was pretreated with supporting electrolyte salts, and the relative humidity of exhaled breath dissolved the preloaded components, thereby activating the electrochemical measurement. Breath thus acted simultaneously as an analyte carrier and activation medium. This study represented the first demonstration of a paper-based electrochemical sensor applied to respiratory analysis and introduced the concept of humidity-driven actuation for breath-phase detection.

Building on this foundational concept, subsequent studies extended paper-based electrochemical sensing to wearable respiratory devices. A notable example is the integration of a paper-based collector within an N95 face mask as a universal sampling solution for airborne biomarkers, including SARS-CoV-2 [48]. In this configuration, the paper-based device served dual functions, capturing virus-containing aerosol particles during respiration and simultaneously acting as a reservoir for subsequent electrochemical analysis of the spike (S1) antigen (Fig. 4B). The detection relied on a magnetic bead-assisted sandwich immunoassay combined with carbon black-modified screen-printed electrodes to monitor the formation of the antigen–antibody complex. In detail, the analytical signal arises from the electrochemical quantification of the enzymatic reaction product, measured by differential pulse voltammetry. Overall, SARS-CoV-2 was captured within the porous matrix during exhalation and subsequently detected electrochemically outside the mask, minimizing direct contact between the user and potentially hazardous reagents. The smart device identified a COVID-19-positive patient with a cycle threshold of 31 using RT-PCR, highlighting its high sensitivity. This approach demonstrated that paper-based electrochemical systems can operate as passive collectors embedded in respiratory protective equipment, enabling safe and scalable breath-related diagnostics.

More recently, Fiori et al. [49] developed a paper-based electrochemical sensor incorporating laser-induced carbon nanofibers decorated with nickel nanocatalysts for aerosolized glucose detection. The sensing element was positioned within the external lateral opening of a breathing mask, enabling direct analyte capture from the aerosol phase. Following sampling, an electrochemical measurement was performed

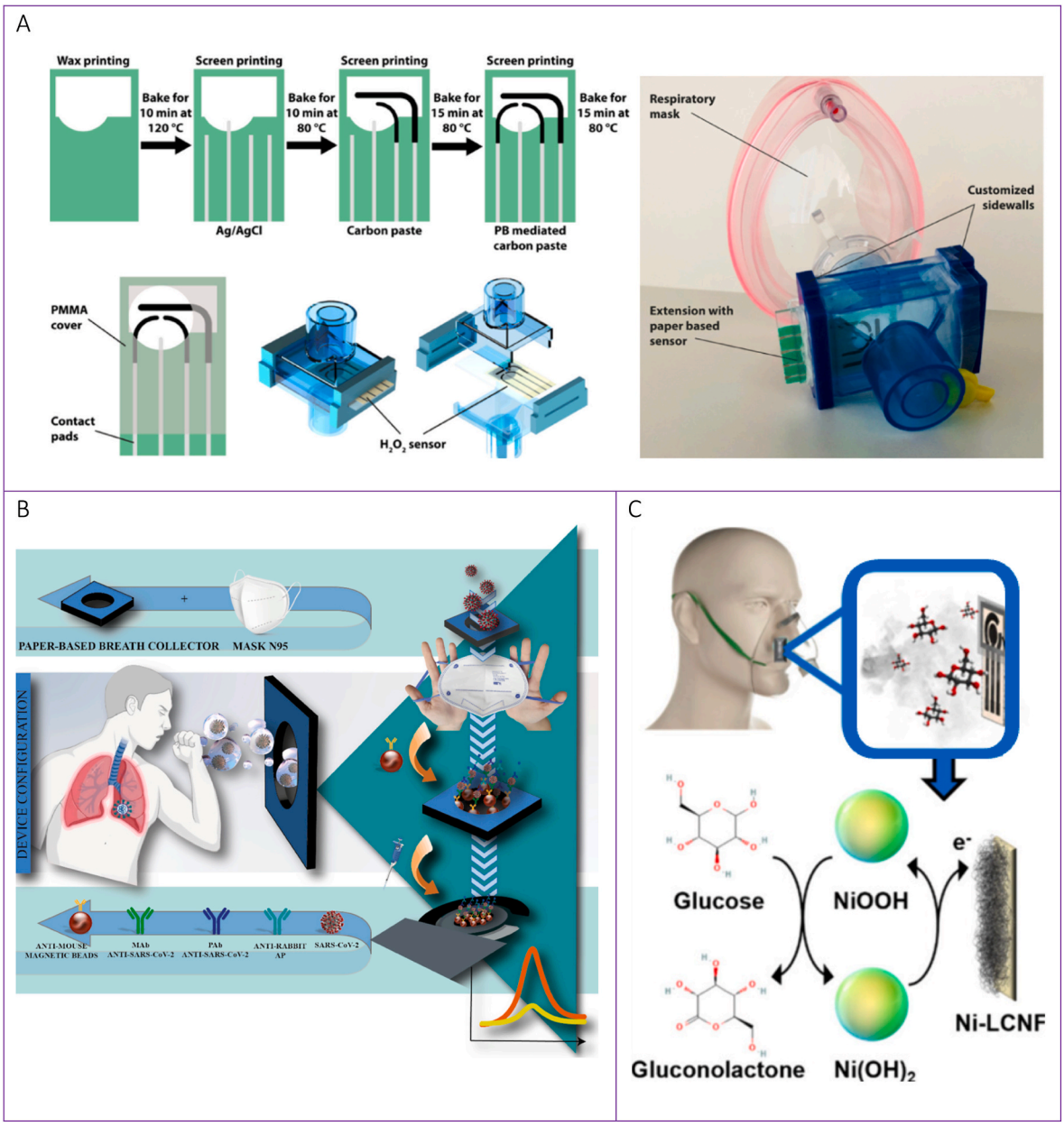


Fig. 4. Paper-based electrochemical wearable (bio)sensors for breath analysis. A) Paper-based analytical device printed with Prussian Blue-modified ink for hydrogen peroxide in breath. Reproduced with permission [47]. B) Paper-based device integrated in a facemask working as a collector and immunoreaction reservoir for SARS-CoV-2 detection in breath. Reproduced with permission [48]. Paper-based device electrochemical sensor based on nickel nanocatalyst for glucose detection in breath. Reproduced with permission [49]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

after activation with an alkaline solution (Fig. 4C). When tested with a nebulized solution, the sensor exhibited a correlation coefficient equal to r = 0.9761 between the glucose present in the nebulization solution and the sensor-captured glucose, demonstrating the reliability of the device integrated into a medical breathing mask.

Overall, extending wearable paper-based electrochemical (bio)sensors for breath analysis underscores the versatility of cellulose as a multifunctional material. By leveraging gas permeability, reagent preloading, humidity-driven activation, and compatibility with mask-based integration, paper-based electrochemical systems open new avenues for non-invasive and low-cost respiratory diagnostics within wearable healthcare paradigms.

4.2. *Agrifood sector*

The extension of wearable paper-based electrochemical (bio)sensors into the agrifood sector illustrates how design principles originally developed for human-centered diagnostics can be translated into plant- and food-interfaced analytical systems. In this context, the term “wearable” expands beyond epidermal devices and includes analytical platforms directly interfaced with plant tissues and food matrices to enable decentralized and real-time monitoring without destructive sampling. The intrinsic porosity, flexibility, low cost, and printability of cellulose substrates make them particularly suitable for such applications, where passive sampling, conformal contact, and field deployability are essential.

A first representative example is the development of screen-printed

electrochemical sensors fabricated on kraft and parchment paper substrates for the real-time detection of carbendazim, a broad-spectrum carbamate fungicide with mutagenic and reprotoxic effects [50]. In this study, a complete electrochemical cell, including working, counter, and reference electrodes, was screen-printed directly onto parchment or kraft paper substrates and subsequently applied to the surfaces of apples and cabbages. The porous structure of kraft paper, in particular, enhanced the effective electroactive surface area and promoted the formation of carboxylic groups upon electrochemical activation, improving analytical performance. After spraying a known amount of carbendazim solution onto the produce and allowing it to dry, the analyte was dissolved using phosphate buffer and quantified by differential pulse voltammetry, yielding recovery values between 96 and 100.8% for apples and from 101.5 to 104.0% for cabbages. Importantly, the device maintained mechanical stability with only 8% signal reduction after 100 bending cycles. This example clearly demonstrates how paper-based electrochemical sensors can operate as conformal wearable-like analytical interfaces directly applied to food surfaces.

Moving from fruit and vegetable-based detection toward in situ plant diagnostics, Parrilla and co-workers [51] developed a 3D-printed hollow microneedle patch coupled with screen-printed electrochemical sensors for monitoring pH, H_2O_2, and glucose in plants (Fig. 5A). In this configuration, the hollow microneedles functioned as minimally invasive sampling probes. By gently pressing the patch, the plant sap was extracted and directed toward a filter paper collecting pad before reaching the electrochemical sensing interface. Individual (bio)sensors were selectively modified by electrodeposition of polyaniline for pH monitoring, Prussian Blue for H_2O_2 detection, and Prussian Blue combined with glucose oxidase for glucose quantification. This approach demonstrates the synergistic integration of additive manufacturing, screen printing, and paper-based fluidics to aid multiplexed plant health assessment directly in vivo, without extensive sample preparation.

Building on the concept of passive environmental interfacing, a flower-like paper-based electrochemical biosensor was designed to monitor the presence of pesticides in the aerosol phase when placed on grass surfaces [52]. In this configuration, a central electrochemical cell printed on office paper was coupled with a filter paper pad shaped into five petals, each preloaded with a specific enzyme (Fig. 5B). The petals acted simultaneously as passive aerosol collectors and biochemical recognition elements. Exploiting enzyme inhibition mechanisms, the system enabled detection of paraoxon, glyphosate, and 2,4-dichlorophenoxyacetic acid at concentrations as low as 2, 10, and 50 ppb, respectively. The porous cellulose structure eliminated the need for external sampling systems, while the origami-based coupling between the enzymatic pad and the electrochemical cell permitted modular and selective analysis, demonstrating how cellulose porosity can be strategically engineered to capture analytes from the aerosol phase and integrate biochemical recognition within a wearable-inspired field device.

Collectively, these examples illustrate the progressive evolution of paper-based wearable electrochemical (bio)sensors from food surface residue detection to aerosol-phase pesticide monitoring and minimally invasive plant diagnostics. By leveraging cellulose porosity for passive sampling, mechanical flexibility for conformal interfacing, and compatibility with scalable printing and additive manufacturing techniques, paper-based platforms redefine the concept of wearable (bio) sensing within agrifood systems. This transition from human health monitoring to plant highlights the versatility of paper as a multifunctional material and reinforces its role in sustainable crop health monitoring.

4.3. Environmental sector

Beyond biomedical and agrifood applications, wearable paper-based electrochemical (bio)sensors are increasingly being explored for environmental monitoring, where decentralized, rapid, and low-cost analytical tools are needed. Environmental matrices including air particulates, solid infrastructures, and water samples, with heterogeneous surfaces that often require adaptable sampling strategies. In this context, the intrinsic porosity, capillarity, and conformability of cellulose substrates support direct interfacing with complex environmental matrices, extending the wearable concept toward e.g. infrastructure contact analytical systems.

A paradigmatic example of aerosol-phase environmental sensing is the origami paper-based analytical device developed in 2019 to detect mustard agents in the aerosol phase when the device is assembled in a soldier's overall. In this system, porous paper pads were preloaded with choline oxidase, the enzymatic substrate choline, and phosphate buffer salts [53]. Environmental humidity acted as a natural actuator, dissolving the preloaded reagents and initiating both the enzymatic recognition process and the subsequent electrochemical transduction. The target in the aerosol phase interacted directly within the porous cellulose network, where the reaction was triggered upon hydration. This work demonstrated that paper-based electrochemical devices can operate directly in the aerosol environment with a detection limit of 0.19 g min/m^3 for real sulfur mustard in aerosol phase. In this way, by exploiting porosity and humidity-driven activation, auxiliary sampling systems and external fluid handling are avoided, delivering a wearable device to be embedded on a soldier's overall for chemical warfare agent detection (Fig. 5C).

Beyond aerosol monitoring, paper-based electrochemical platforms have also been successfully applied to solid environmental matrices, particularly in infrastructure diagnostics. Colozza et al. [54] developed a vertical-flow paper-based sensor for on-site evaluation of chloride contamination in concrete structures. In this configuration, cellulose porosity enabled controlled vertical transport of the extracted chloride ions from the concrete surface through the paper matrix to the electrochemical detection zone (Fig. 5D). The vertical-flow architecture provided reproducible mass transport and minimized analyte dispersion, allowing for rapid and reliable quantification directly on structural materials as demonstrated in in-field measurements at the Giacomo Manzù Museum (Ardea, Italy), which is located about 6 km from the coast and thus exposed to a chloride-rich marine environment.

Similarly, Colozza et al. [55] reported a paper-based screen-printed Ag/AgCl electrode that can be placed directly on concrete surfaces for corrosion assessment. Corrosion was determined by monitoring the potential difference between the embedded steel reinforcement and the paper-based screen-printed Ag/AgCl electrode, requiring only 70 μL of electrolyte to establish electrical contact. Compared with the standard method, which uses a half-cell potential test with a bulk reference electrode connected to the concrete surface via a wet sponge, the paper-based device eliminates the need for both the wet sponge and the bulky reference electrode (Fig. 5E). In this configuration, the wet sponge is replaced by a paper pad wetted with only 70 μL of electrolyte, while the bulky reference electrode is replaced by a paper-based screen-printed reference electrode. The device performance was validated under controlled laboratory conditions using reinforced concrete specimens and subsequently in a real-world scenario on the outdoor sculpture *Music Collection Session* by Arman (Milan, Italy).

Collectively, these examples illustrate how paper-based electrochemical devices can transition from aerosol-phase detection to direct solid infrastructure monitoring. By leveraging porosity for passive extraction, capillarity for controlled transport, and conformability for surface interfacing, cellulose substrates allow for decentralized environmental diagnostics beyond conventional liquid-sample analysis. The extension of paper-based wearable concepts from biological to environmental and structural contexts further underscores their versatility as multifunctional analytical tools that support sustainable surveillance of infrastructure.

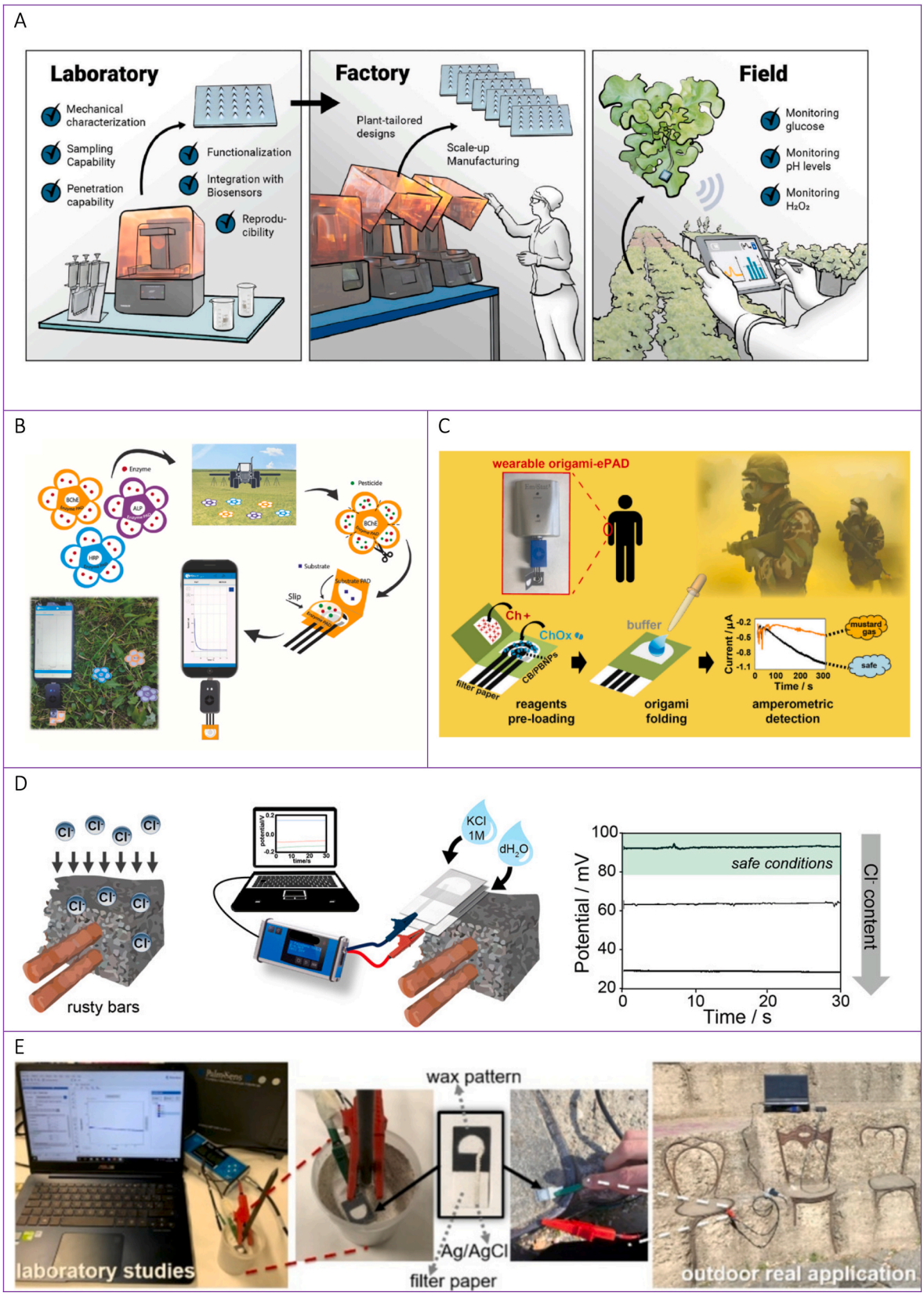


Fig. 5. Paper-based wearable electrochemical (bio)sensors for target analyte detection in plant, aerosol, and concrete solid structures. A) 3D-printed hollow microneedle patch combined with screen-printed electrochemical sensor and paper-based pad for monitoring pH, H_2O_2, and glucose in plants. Reproduced with permission [51]. B) Paper-based electrochemical flower-like origami working as a wearable device on soil for customized pesticide use. Reproduced with permission [52]. C) Wearable choline-oxidase origami paper-based device on the soldier's overall for the detection of mustard agent in the aerosol phase. Reproduced with permission [53]. Paper-based electrochemical potentiometric sensor for the detection of chloride contamination (D) [54] or corrosion level (E) [55] in concrete structures. Reproduced with permission [54,55].

5. Conclusions

Wearable paper-based electrochemical (bio)sensors have moved beyond the concept of simplified analytical tools and have recently evolved into structurally engineered systems capable of addressing decentralized healthcare, agrifood monitoring, and environmental surveillance. Their significance does not lie in merely substituting polymeric substrates for cellulose, but in deliberately exploiting the intrinsic properties of paper, including porosity, capillarity, foldability, breathability, and mechanical robustness as governing design principles. In this framework, paper is no longer a passive support, but an active structural material that dictates fluid dynamics, assay architecture, and system integration.

The transition from academic prototypes to analytical tools with Technology Readiness Levels (TRLs) 7–9 depends on overcoming critical limitations in manufacturing reproducibility, limited stretchability under dynamic mechanical stress, and the still-evolving regulatory framework for paper-based wearable systems applied in the healthcare field. The relevant critical challenge for the clinical translation of wearable paper-based electrochemical (bio)sensors is the validation and acceptance of alternative biofluids, particularly sweat, as reliable diagnostic matrices. While numerous biomarkers have been proposed for sweat-based monitoring, their clinical relevance and correlation with established blood or laboratory measurements still require extensive validation across large patient cohorts. To date, the only accepted clinical application of sweat analysis remains the diagnosis of cystic fibrosis through sweat chloride determination, which is considered the gold standard. However, this procedure does not rely on continuous wearable monitoring, as sweat is pharmacologically stimulated by pilocarpine iontophoresis and then collected for analysis. Therefore, the successful translation of wearable sweat (bio)sensors will depend not only on technological advances but also on strong clinical evidence demonstrating the diagnostic significance, robustness, and medical utility of sweat-derived biomarkers. Addressing these issues is not a marginal refinement but a necessary step toward technological widespread adoption.

Future developments should therefore focus on standardized fabrication strategies, improved mechanical design to accommodate dynamic deformation, and system-level integration between disposable paper-based sensing interfaces and reusable electronic modules. Furthermore, leveraging established industrial concepts, such as dry-reagent storage and compartmentalization strategies successfully used in colorimetric lateral flow assays, together with sustainable manufacturing processes and modular wireless architectures, may accelerate the translation of paper-based wearable electrochemical (bio) sensors into commercially viable products.

By merging intrinsic material simplicity with rational engineering and wireless connectivity, these analytical tools are positioned to contribute significantly to the evolution of decentralized and integrated analytical systems for the next generation of smart and sustainable wearable devices. Ultimately, future success will depend not only on achieving excellent analytical figures of merit but also on balancing performance with manufacturability, reproducibility, user comfort, cost-effectiveness, sustainability, and regulatory compliance, thereby enabling the widespread adoption of wearable paper-based electrochemical (bio)sensors in real-world applications.

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.

Acknowledgements

PRIN2022 project SMARTMASK4CF, the Horizon Europe COP-PILOT project, grant agreement 101189819 and Healthy Soldier, Italian Ministry of Defence.

Data availability

Data will be made available on request.

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