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Review—Flexible and Stretchable Electrochemical Sensing Systems: Materials, Energy Sources, and Integrations

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This review details the key progress made on flexible and stretchable electrochemical sensing systems, along with their relevant challenges and opportunities for the future. Stepping forward from traditional rigid electrodes, recent advancements in non-rigid electrochemical sensors offer new and exciting opportunities for various applications, such as biomedical, fitness, or environmental monitoring. The key factors in developing such devices are the materials and integrated systems needed to retain mechanical compliance while maintaining electrochemical functions. This requires a devotion to judiciously engineer both the underlying substrates and electrode materials. However, the realization of compliant electrochemical sensing devices still faces many obstacles. The requirements and potential strategies to enable flexible and stretchable electrodes are further discussed in this review. In addition to such sensing units, which mainly consist of electrodes and functionalized transducers, integrated systems also require miniaturized viable and mechanically compliant energy sources, as well as low-power electronics for controlling the device and wirelessly communicating with users. Such advancements, alongside other attractive functionalities such as self-healing and transparent properties, are also discussed. The innovative flexible and stretchable sensing systems will extend a variety of non-invasive, minimally invasive, wearable, and implantable applications to patients. Examples of compliant sensing systems and relevant challenges are included alongside perspectives of this emerging technology.
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Flexible and stretchable biosensors and bioelectronics have become emerging technologies for many useful and versatile applications, in particular biomedical applications.[1–4] Apart from electronics that track physical parameters (such as strain[5] and electrocardiograms[6]), electrochemical sensing is one of the most significant types of flexible and stretchable sensing systems that allows for unique opportunities to monitor comprehensive chemical information (such as presence/concentration of glucose,[7] lactate,[8,9] dopamine,[10,11] cortisol,[12] and drugs[13]). Unlike traditional rigid electrochemical sensors, flexible and stretchable sensors offer a unique potential to interface with human skin or the curvature of soft biological materials, significantly improving detection performances for monitoring biomarkers, electrolytes, drugs, or various biomolecules.[14,15] Mechanically compliant electrochemical sensors hold great capabilities for wearable and implantable technologies (e.g., for brain,[16] tissue,[17] and cells[18,19]). Integrating mechanically compliant properties into electrochemical sensing systems can also complement applications in the modern internet of things (IoT). With integrated sensing systems, users, big data, integrative diagnostic, and therapeutic processes are linked to advance the quality of modern life. Moreover, soft electrochemical sensors could open opportunities to explore new deep studies in biomedical research (such as biochemical signals induced by mechanotransduction[20]) that rigid platforms could not offer. Apart from such biomedical applications, soft sensing systems also hold considerable attention for human-machine interfaces in soft robots or human-like robots.[21]

Flexible, stretchable, and electrochemical sensing systems consist of many units. For practical biomedical or soft robotic applications, isolated flexible and stretchable electrodes are not enough. These integrated systems also require energy and controller units. The main components of flexible, stretchable, and electrochemical sensing systems include the sensor and electrochemical transducer, energy supply, and electronics (Fig. 1). The first bottleneck is a limitation of viable materials for supporting conductivity in the electrodes and underlying substrates. While electrodes on soft substrates must be robust and mechanically resilient, they also need to be suitable electrochemical transducers capable of supporting platforms for the functionalization of active layers, such as biorecognitions, mediators, or catalysts. Another challenge lies in the rigidity, bulkiness, and low power density of energy sources, making the components incapable of incorporation with final electrochemical sensing systems. Developments in new viable soft energy sources, including both energy-harvesting and energy-conversion devices, are becoming a grand interest in the scientific community to further push progress in the areas of flexible and stretchable bioelectronics. A third limitation exists in controlling electroanalytical sensors while communicating between the sensors and users.[22] Exceptional attention must be given to translate existing rigid electrochemical instruments into new and fully integrated compliant systems. Developing materials and electrochemical systems for biosensors and bioelectronics could enhance the amenity of next-generation biomedical sensing devices. Our goal is to discuss some key challenges covering these three important components, along with potential strategies to fill the gap of the key requirements, in the following sections.

According to all databases from Web of Science (accessed early 2020), the number of publications in the field of electrochemical sensors from 1980 to 2019 has exponentially increased. We have further investigated the relevant topics of (1) flexible and (2) stretchable electrochemical sensors. The resulting graphs are shown in Fig. 2. We also estimate the relative percentages of publication numbers in the topical terms "flexible" or "stretchable electrochemical sensors" with respect to the number of overall "electrochemical sensors" by using the following formula: $Percentage_{Flex.\ electrochem.\ sens.}$ and $Percentage_{Stretch.\ electrochem.\ sens}$ are defined as $N_{Flex.\ electrochem.\ sens.}/N_{Electrochem.\ sens.}$ *x 100% and* $N_{Stretch.\ electrochem.\ sens.}/N_{Electrochem.\ sens.}$ *x 100%,* where $N_{Electrochem.\ sens.}$, $N_{Flex.\ electrochem.\ sens.}$, and $N_{Stretch.\ electrochem.\ sens.}$ are number of publications when searching by using the topic terms *"Electrochemical Sensor," "Flexible Electrochemical Sensor,"* and *"Stretchable Electrochemical Sensor,"* respectively. As shown in Fig. 2 (right), we found an increase in percentages of publication numbers in the topic terms of "flexible electrochemical sensors" or "stretchable electrochemical sensors" with respect to the number of

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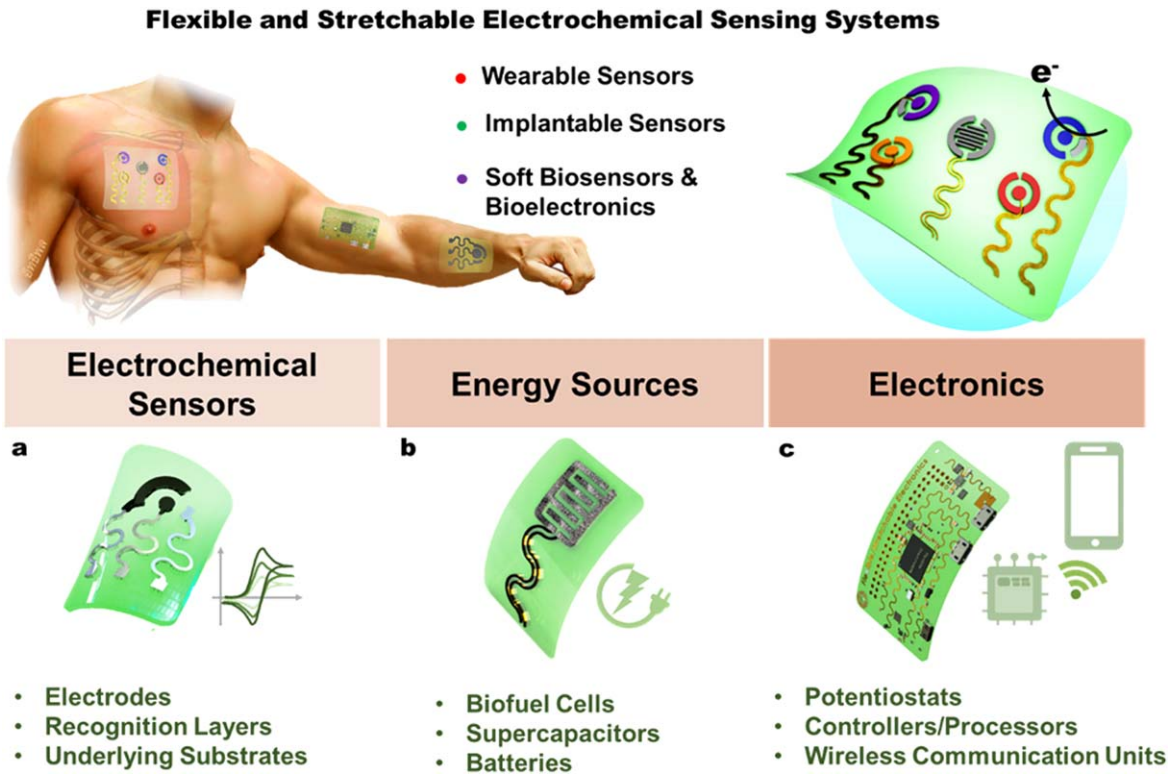

Figure 1. Conceptual illustration of flexible and stretchable electrochemical sensing systems that allow key capabilities for biological material–sensor interface in biomedical applications, such as wearable and implantable platforms. The flexible and stretchable electrochemical sensing systems consist of (a) sensors; (b) energy sources; and (c) electronics.

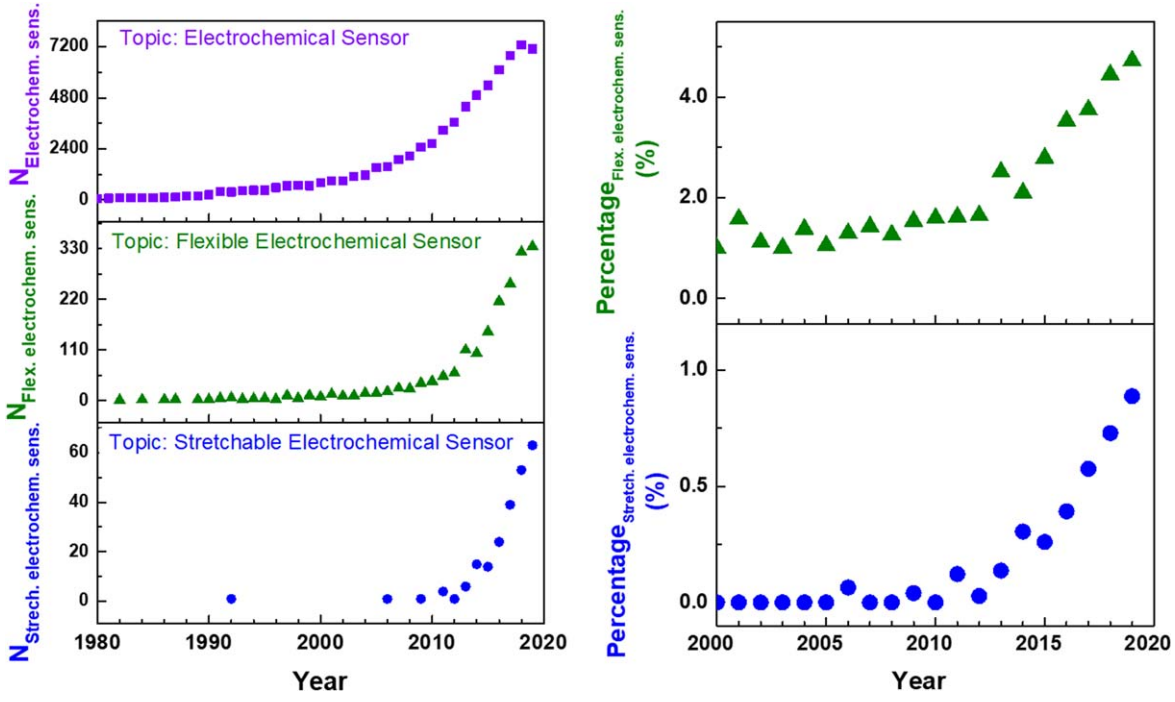

Figure 2. Graphs of a search on the topic terms "Electrochemical Sensor," "Flexible Electrochemical Sensor," and "Stretchable Electrochemical Sensor" during the period 1980 to 2019, using the Web of Science.

overall "electrochemical sensors," indicating the importance and interest of such emerging fields. This clear trend started in ∼2013. Note that the field of stretchable electrochemical sensors has only recently emerged, compared with the relatively older topic of flexible electrochemical sensors.

In this article, we review key advances in flexible and stretchable electrochemical sensing systems. The focus of this article aims to discuss some significant challenges in the fields, rather than collect the details of existing research or describe fundamental principles of electrochemical sensing systems. This comprehensive and basic

information can be found in earlier references.[3,23–26] Grander challenges related to the following significant components are highlighted in our article: (1) flexible and stretchable electrochemical sensors, which consist of soft underlying substrates and conductive electrodes along with their surface for electrochemical transducers; (2) energy sources; and (3) flexible and stretchable electronics. In addition, new supplementary properties for electrodes, such as self-healing and transparency, for revolutionary flexible and stretchable sensors are discussed. We also add viewpoints emphasizing key challenges that the development of integrated flexible and stretchable electrochemical sensing systems encounters and potential strategies to address grand obstacles. Besides examples in the emerging field of such compliant sensing systems and relevant challenges, outlooks of this exciting technology for multiple purposes, mainly for biomedical sensors, personalized healthcare, or human–machine interfaces in soft robotics, are also summarized with respect to addressing challenges and exploring new applications.

Meeting Challenges Related to Materials for Flexible and Stretchable Electrochemical Devices

With an increasing demand for flexible and stretchable biosensors and bioelectronics, efforts have been devoted towards developing a class of sensing devices that are lightweight, flexible, stable in long-term, and sensitive to electroanalytical parameters. The choice of materials is critical to achieve these desirable standards. In this section, several materials commonly used for the fabrication of stretchable sensors will be discussed. Two main fundamental components needed for building up flexible and stretchable electrochemical sensors include (1) underlying substrates and (2) conductive electrode materials.

Underlying substrates.—The selection of the underlying substrate is key to making a flexible and stretchable device since the overall features of sensing systems depend on the nature of the substrate. The degree of bendability, foldability, and stretchability determine the conformable integration of substrates into non-planar/soft surfaces, which is the core obligation of soft electronic systems. General requirements for underlying supports are lightweight functionality, ultra-conformability, portability, disposability, and inexpensive cost.[27] The adhesive between the sensing material and substrate is also one of the primary considerations in the overall stability of the sensing system. This issue relies on both the substrate and the conducting material. A surface-energy mismatch between active materials and substrates can cause unsatisfactory surface homogeneity in the sensors. The devices fabricated on three types of substrate candidates, plastic, elastic, and textile, are further discussed in this section.

Obstacles when using flexible plastic substrates.—Polymeric substrates are candidates for disposable or low-cost sensors due to flexibility, low weight, availability, and affordability. Compared to inorganic crystalline materials, e.g., silicon, most polymers are more flexible. Common polymeric substrates are polyethylene naphthalate (PEN),[28] polyethylene terephthalateble (PET),[29,30] and polyimide (PI).[31,32] Considering some drawbacks in their mechanical and chemical characteristics, the decision to utilize a material relies on their suitability for a particular application. For example, PI is often used in situations involving high temperatures and harsh conditions due to its high resistance to heat and external mechanical force[31]; however, it turns yellowish owing to the formation of intra- and/or intermolecular charge transfer complexes. Polycarbonate and polypropylene adipate can also be severely damaged at high temperatures. Polyethersulfone absorbs moisture readily and turns yellowish as well.[33]

The common issue of many plastics is poor adhesion, significantly limiting their applications and commercialization. Furthermore, polymeric films are typically sensitive to high temperatures; therefore, processes for manufacturing are limited to only low-temperature processes, i.e., normally lower than 200 °C. Annealing is normally required for printing techniques since the removal or decomposition of organic materials from the substrate is necessary to establish a continuous and conductive network throughout the electrode; however, cracking due to the large reduction of the intrinsic volume may result in weak adhesion with the substrate and poor cohesion within the electrode layers. This causes an adverse increase in electrical resistance.[34] By using nanosized glass frit as an adhesion promoter for inkjet-printed conductive material, a crack-free dense microstructure of Ag patterns could form and adhere well to substrates. Unfortunately, this technique requires high-heat treating temperatures (∼500 °C) undesirable for common plastic substrates, such as PET and PI.[35] Hence, the formulation of ink needs to be considered, and will be discussed in following sections regarding the limitations of screen-printing and inkjet-printing approaches. To avoid high-temperature treatment, localized treatment is developed. Intense pulsed light irradiation is an example of an approach used to implement annealing. For example, pulsed light irradiation was used to remove organic species present on the surface of copper nanowires (CuNWs) and to form direct connections between the NWs, allowing self-nanoembedding of the conductive electrode into a plastic substrate.[36] The use of this conductive copper ink showed high conductivity of printed copper patterns as well as enhanced adhesion to the PI substrate.

Obstacles when using stretchable substrates.—Stretchable elastomers, such as polydimethylsiloxane (PDMS), are often used as soft substrates. PDMS is useful due to its hydrophobicity, chemically inert state, and biocompatible nature. However, without pretreatment of the elastomer, normal patterning inks cannot strongly adhere to PDMS, presenting a difficulty in depositing conductive tracks directly on PDMS.[37,38] To address this issue, several approaches have been reported, such as using a coupling agent to ensure the chemical adhesion, and strengthening the bonding between conductive inks and elastomeric surfaces. Examples of these routes include the spraying of a primer or printing a gluey layer. When using PDMS as the substrate, a typical alternative is a film transfer process from a patterned template or mold to receiving PDMS. Normally, Si or glass is used as the release substrate. In this strategy, a pre-patterned glass substrate was first deposited with an active material, e.g., a silver nanowire (AgNW) solution. Then, the top of the AgNW layer was coated by liquid PDMS. Finally, the AgNW/PDMS film was peeled off from the glass substrate to complete the film-transfer process. With the sensing material embedded, the adhesion between AgNWs and PDMS significantly affected the transfer efficiency of AgNWs from the release substrate. The AgNW/PDMS electrodes showed both high conductivity ($R_s = 14\ \Omega\ sq^{-1}$) and optical transmittance ($T = 90\%$). [39] Instead of using a flat substrate, a buckle formation of PDMS surface was also applied as a mold. This alternative can be prepared by treating pre-stretched PDMS (40% strain) with ultraviolet/ozone radiation to introduce a thin film of silicon oxide on the PDMS surface. AgNW solution was then coated onto the PDMS mold. The PDMS mold was released to its initial length (zero strain), and the buckled AgNW film was obtained. The purpose of this technique is to achieve "wavy" shapes of metallic interconnects. The liquid PDMS with a curing agent was poured on the buckled AgNW film. Due to the penetration of the liquid PDMS into the AgNW network, the AgNW film was embedded tightly into the cured PDMS; the PDMS mold was eventually peeled off. The resulting resistance of embedded AgNWs (45 Ω) was slightly higher compared to the resistance of the AgNWs film (20 Ω), and the conductivity of the AgNWs film improved after releasing strain (25 Ω) due to the rearrangement of AgNWs and their electrical junctions.[40]

Another approach to further improve the stretchability of the PDMS substrate is leveraging soft lithography to generate three-dimensional (3D) micropatterns to obtain continuously arranged and

curvilinearly connected architectures. In this pattern, bumps and valleys are regularly positioned in hexagonal closed packed structures, generating a wavy structure and offering multidirectional stretching capability. Such 3D micropattern structures on the substrate surface can effectively absorb the strain of the electrode materials during stretching. This enables the use of conventional fabrication processes and electrode materials, such as thin metallic electrodes and a Ag/AgCl reference electrode. An example stretchable electrochemical sensor composed using these techniques could be elongated up to 30% without loss of electrochemical characteristics.[41] After 1000 stretching cycles at an elongation of 30%, the fabricated sensor also showed a sensing performance similar to that of the initial performance, indicating durability.[41] Recently, surface treatment with oxygen plasma was also used to prepare deformable conductive patterns or devices directly on the surface of PDMS. This plasma treatment can temporarily render the surface into a hydrophilic surface.[42] The obtained printed tracks exhibitedstrong mechanical stability and a high electrical conductivity under bending, twisting, and stretching distortions.[43]

Apart from using PDMS, polyurethane (PU) and temporary tattoos are also employed.[7,44] On a polyurethane/Ecoflex substrate, a printed CNT layer withstands large levels of strains (up to 500% strain) with negligible effect on its structural integrity and performance.[44] Since polyurethane has high porosity, it can also act as a semipermeable membrane. This allows the integration of a PU substrate and conductive gold patterns for stretchable and breathable skin-inspired biocompatible sensors.[45] The semipermeable polyurethane films had a pore size larger than air and water vapor molecules but smaller than liquid water droplets and bacteria. As such, the fabricated sensor was permeable with outside air and water vapor while being impermeable to water and bacteria.

Obstacles when using textile substrates.—Textiles are among the most attractive candidates for substrates since it is convenient to syndicate electrodes with common clothing for various applications, in particular for wearables.[46,47] However, using textiles as underlying substrates causes several challenges that should be addressed. The curing condition becomes challenging because a high sintering temperature, in general, is needed to help solvent evaporation, and importantly to ensure the strong attachment of electrode materials on the textile surface. High temperature produces negative effects on the substrate, including mechanical deformation or loss of tensile strength. Alternatives for sintering, such as laser and microwave flash techniques,[48] can minimize the processing temperature; however, they rely on expensive and complicated setups, and are therefore less viable for mass fabrication. In order to address this obstacle, new recipes of conductive inks that allow low processing temperatures need to be developed.[49] An example of this is AgNPs (diameter of 10 nm), which could be dispersed in aqueous solution. The addition of HCl and polyaniline would help to enhance the adhesion and lessen oxidation issues. A low temperature of 60 °C for 30 min was able to cure the ink and allow strong bonding on cotton substrates. Another challenge is the rough surface of typical textiles, resulting in poor uniformity of the ink patterning (such as providing disconnected conductive traces of electrodes and deteriorating mechanical properties). To improve the quality of electrodes attached to the textile, smoothening of the textile surface is necessary. An example of this strategy is using laminating polymeric sheets, which could be applied on the rough textiles prior to the successive fabrication of electrodes.[50,51] Another strategy is using vapor-phase organic chemistry to create conductive materials on the porous textile.[52] Even though the textile surface is still rough, this technique allows the direct coating of a conjugated polymer film to fabricate various conductive components. Advantageously, such a direct deposition eliminates the requirement of pretreating processes, thus enabling simplicity while maintaining the breathability of the fabric.

Conductive materials for underlying flexible and stretchable electrodes: meeting challenges in fabrications.—The choice of conductive materials is a core issue to be explored. General requirements for electrode materials in electrochemical sensors are high conductivity, a suitable electrochemical potential window, and good catalytic activity. Most importantly, active materials must be flexible and stretchable. In many cases, electrode materials should provide a functional group for the immobilization of biological elements, such as enzymes, proteins, or antibodies. Thus, rational designs of functionalized electrodes need to be developed. For instance, some materials, e.g., carbon electrodes, normally need to be activated to generate the carboxylic group for the subsequent functionalization with an 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/N-hydroxysuccinimide (EDC/NHS) coupling before enzyme or protein immobilization via covalent bonding.[53] Various methods have been applied to manufacture mechanically compliant electrodes; the most common method is the deposition of conductive materials onto the surface or embedding them inside a substrate/matrix. Stretchable systems are also achieved by engineered shapes, such as connected islands, where the opening and enlargement of cracks can relieve most of the strain. Moreover, nanomaterials can be patterned into horseshoe, filamentary serpentine, or fractal shapes to accommodate the strain.[54,55] The following sections will focus on strategies for sensing electrodes.

Limitations of casting and coating approaches.—Direct coating and deposition methods, including drop casting, spin coating, dip coating, and spray coating, are among the easiest routes to prepare flexible and stretchable electrodes. Drop casting can be done simply by depositing a droplet onto the substrate and letting the solvents evaporate. The concentration of the solution plays an important role in the film thickness. To improve reproducibility, spin coating/casting can produce uniform films over a large area. In dip coating, the substrate is dipped into the solution, and then withdrawn at a controlled speed. Thickness is determined by the balance of forces at the liquid-substrate interface. It should be noted that it is challenging to pattern the desirable electrode design when employing such simple coating approaches. An alternative to address this obstacle is to utilize a mask or stencil.[56,57] For example, the sensing material was simply drop-casted on the pattern. As shown in Fig. 3a, three layers of an electrochemical glucose sensor are fabricated by spin casting and drop casting approaches. The first layer, the active material of reduced graphene oxide, is spin-casted on the patterned gold patch, followed by drop-casting of an enzymatic layer over the prepared layer of reduced graphene oxide, and finally a top layer of Nafion.[53] However, with the drop-casting process, cracking due to misfit stress between the precipitate crystal and the ultrathin film is usually observed. This cracking can be minimized by introducing pores on the ultrathin-film surface to release the stress (Fig. 3b).[58]

Weak interactions between sensing materials and substrates always cause peeling of the electrodes and severe cracking of sensors under stretching.[63] For example, a relatively low adhesion force due to weak van der Waals forces and a limited contact area are normally observed in the cast of coated AgNWs on the substrate. Thus, AgNWs were easy to detach from the substrate during mechanical deformation. The adhesion can be improved by mixing with ionic liquids and polymers.[64] The transparent electrodes made of metal NWs are normally prepared via this approach; however, the addition of polymers significantly decreases the conductivity of the composite film, making it challenging to choose an appropriate polymer. The type of polymer suitable for the sensor application is a matrix polymer with a high Poisson's ratio because under stretching, the change in total volume can be lessened.[65] Polymeric aerogels are also used as the transfer medium to fabricate flexible and transparent AgNW electrodes. The high surface-to-volume ratio of aerogels ensures a strong van der Waals interaction between AgNWs and aerogels. Therefore, an efficient process for transferring films was implemented due to the stronger van der Waals interactions formed

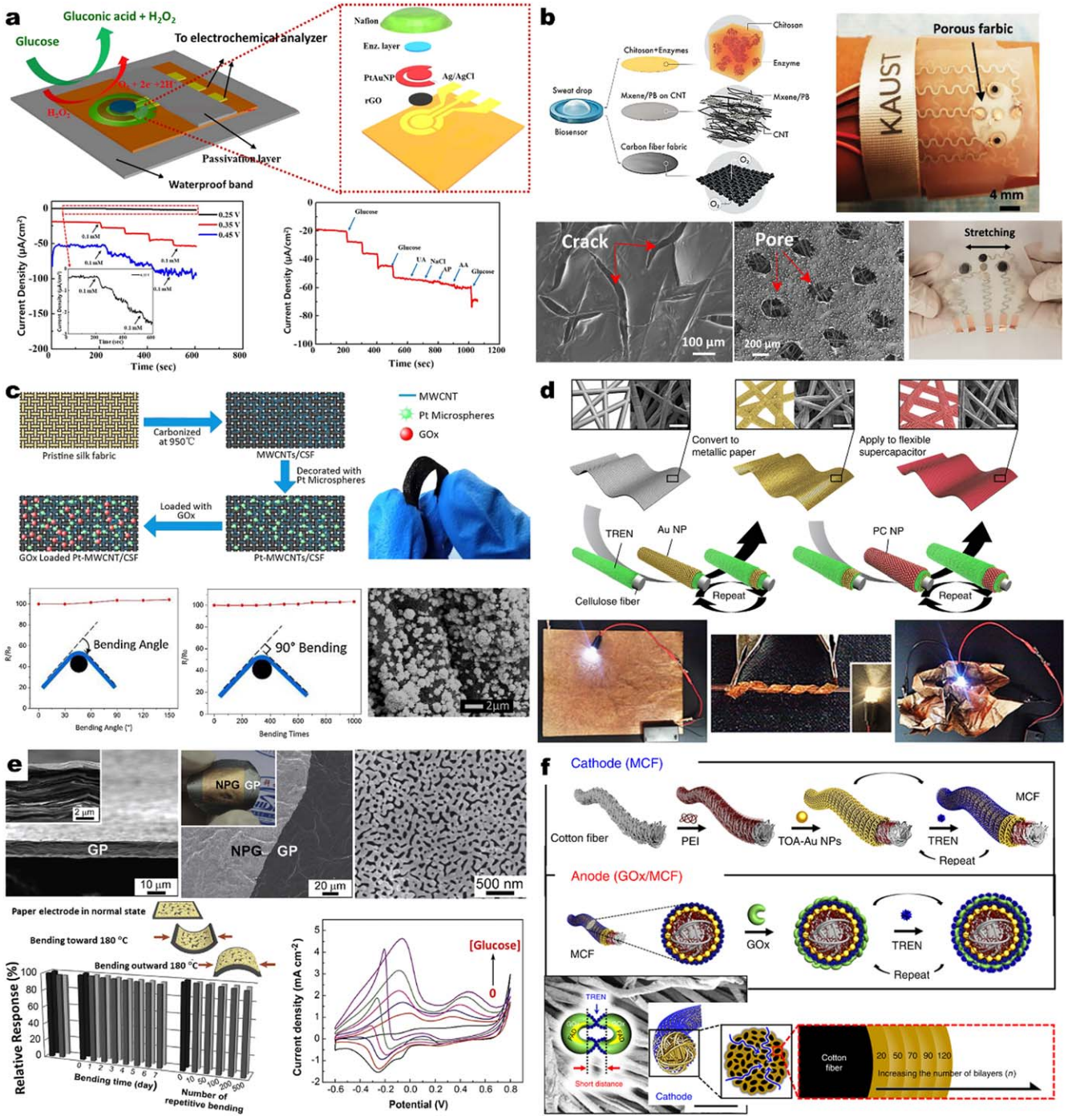

Figure 3. Examples of applications utilizing the casting and direct growth approaches for flexible and stretchable electrodes. (a) The wearable sweat-based glucose biosensor. Adapted with permission,[53] Copyright 2018, Elsevier. (b) The wearable sweat monitoring of pH, lactate, and glucose concentrations. Adapted with permission,[58] Copyright 2019, John Wiley and Sons. (c) Flexible electrochemical glucose sensors based on CNTs/carbonized silk fabrics decorated with platinum microspheres. Adapted with permission,[59] Copyright 2018, Elsevier. (d) Flexible supercapacitor electrodes based on real metal-like cellulose papers. Adapted under the terms and conditions of the CC-BY,[60] Copyright 2017, Ko et al., published by Nat. Commun. (e) Freestanding and flexible Pt-Co alloy nanoparticles/3D nanoporous gold scaffold supported on graphene paper electrode for glucose sensors. Adapted with permission[61] Copyright 2016, Elsevier. (f) High-power hybrid biofuel cells (BFCs) using layer-by-layer assembled glucose oxidase-coated metallic cotton fibers. Adapted under the terms and conditions of the CC-BY,[62] Copyright 2018, Kwon et al., published by Nat. Commun.

by aerogels between AgNWs and the polymer substrate over those between AgNWs and the silicon release substrate, thus promoting the desirable detachment of the AgNWs from the release substrate during embedding.[64] Embedding AgNWs below the surface of PDMS could create stretching and release the AgNW/PDMS composite. The observed conductivity was ~8,130 S cm^{-1} (sheet resistance of 0.24 Ω sq^{-1}) before stretching. After a few stretching/releasing cycles, the resistance of our AgNW/PDMS conductor remained stable in the tensile strain range of 0%–50%, with a high conductivity of 5285 S cm^{-1}.[66]

Another example that improves the stretchable capacity is the embedding of silver-gold (Ag-Au) core-sheath nanowire networks in the surface layer of a poly(styrene-butadiene-styrene) elastomer, instead of normal drop casting or spin coating. The interpenetrated

Ag-Au core-sheath nanowire networks and the cross-linked polymer matrix resulted in stretchable electrodes with high surface conductivity (41,850 S cm^{-1}, at 0% strain) and rubbery elasticity (stretchability of ~266% with a maximum of 840%).[6] The aggregation of nanomaterials during the mixing or curing process dramatically impairs the interaction with the matrix, resulting in concentrated stress at interfaces. The improvement of dispersion techniques with ultrasonication, shear mixing, and hot-rolling processes would ensure the uniform distribution of the conductive filler material, enhancing long-term reliability. The direct growth of active materials on flexible substrates (e.g., carbon fiber,[62] carbon cloth,[67–69] silk fabric[59]) is also an alternative strategy for improving long-term stability in flexible and stretchable electrodes. The direct growth of active material on substrates also overcomes the drawbacks of mixing active electrode materials with conductive additives and binders, which hinder electron transport from nanostructure material to the electron transfer.[70] Furthermore, the direct growth of material on the supporting substrate offers 3D network structures, providing open channels for efficient electron/ion transport and a large surface area for reactions; both are favorable for electrochemical devices (Figs. 3c–3d).[60] For instance, performing electrodeposition of Pt-Co alloy on a nanoporous gold scaffold supported on graphene paper yielded highly dense, well dispersed, and ultrafine nanoparticles. With high mechanical strength and good adhesion among Pt-Co nanoparticles, nanoporous Au film, and graphene paper substrate, this sensor setup maintained a good amperometric response while bending inward or outward to angles of 180° (Fig. 3e).[61]

For bioelectronics, in most cases, enzymes have been directly deposited onto the sensing layer through conventional physical adsorption. The limited control of the interfacial distance, conformation, and stability between the enzyme and the conductive support represent other challenges. Layer-by-layer (LbL) assembly methods offer effective opportunities to prepare conductive multilayer films with tailored thickness, functionalities, and compositions on substrates of various sizes and shapes by utilizing complementary interactions. To build up multilayers, bulky insulating polyelectrolytes are generally applied. Unfortunately, the mutual electron transfer is significantly suppressed due to increased contact resistance.[71] Therefore, the ideal strategy would be to replace bulky polymer electrolytes with small-molecule linkers, such as tris-(2-aminoethyl)amine (TREN). The amine groups of TREN can covalently adsorb on the surface of gold nanoparticles (AuNPs) due to their strong affinity. In this example, tetraoctylammonium bromide-stabilized AuNPs (TOA-AuNPs) were then coated on cotton fibers. Negatively charged glucose oxidase enzyme was LbL-assembled electrostatically onto the TOA-AuNP/TREN cotton fibers due to the positively charged TREN, providing 3D spatial arrangement without agglomeration, and facilitating electron and ion transport for the efficient electrocatalytic reaction on the high conductive platform (>2.1 × 10^4 S cm^{-1}) (Fig. 3f).[62]

Limitations of screen-printing approaches.—Patterning is crucial for the fabrication of electrodes. Patterning electrode sensor materials can be achieved through thin-film microfabrication and thick-film screen-printing methods. The former will be discussed further in the section of limitations of photolithographic approaches. Despite the many advantages of thin-film microfabrication, a big challenge in photolithographic techniques is the limited choice of materials, especially biomaterials, in order to fabricate biosensors that should be vacuum-deposited and stable in extreme conditions. Screen printing becomes an alternative that can also create a thick film in a μm range in a single printing pass. To achieve successful flexible and stretchable electrochemical devices, functional inks become the lifeblood of printed electronics. Inks can be conveniently modified to build compliant electrochemical sensors with engineered surface chemistry. For instance, stretchable screen-printed carbon electrodes could be functionalized with ionophores to fabricate potentiometric sensors.[72] Moreover, carbon electrodes can be screen-printed on several substrates for the development of first generation biosensors, which quantifies the analyte by the amperometric oxidation of H_2O_2. In addition, carbon-based electrodes enable the direct detection of heavy metals and electroactive species, e.g., by square wave voltammetry.[73,74] It should be noted that carbon-based materials are most conveniently printed rather than sputtered. Ag/AgCl is also commonly used as the reference electrode due to its ease of printing.[75] Recently, stretchable and screen-printable Ag/AgCl ink for a variety of substrates, such as stretchable polymers and textiles, was also demonstrated, facilitating the fabrication of compliant electrochemical sensors.[8,44] Advantageously, the screen-printing approach is able to add extra customized catalysts and elastomers into the screen-printable ink.This serves toenhance signals in conformable enzymatic electrochemical sensors, and to shift the applied potential, minimizing interference effects due to co-existing electroactive species. One example is using synthesized platinum-decorated graphite dispersed with the binder, offering stretchable screen-printable ink with catalytic functions (Fig. 4a).[7] The added platinum catalyst could enhance the electrocatalytic reaction for electrochemical sensing tasks. Alternatively, the overpotential required for the detection of H_2O_2 can be decreased by integrating chemicals (such as Prussian Blue[75,76] and Berlin Green[77]) in the ink composition during construction of flexible biosensors as shown in Fig. 4b. Fundamentally, these H_2O_2 sensing capabilities are useful for many biosensing systems. Moreover, the redox enzyme can be integrated into the modified ink for the fabrication of second-generation biosensors, where the redox mediator act as an electron-shuttle assistant. CNTs,[78] nanowires,[79] gold,[80] conductive polymers,[81] metal oxides,[82] and nanocatalysts[83] are also commonly used inactive recognition layers or to improve the performance of biosensors (Figs. 4c–4d).

Dispersed noble-metal nanoparticles, such as gold and platinum, have been used for screen-printed electrodes owing to their good electrical conductivity and inertness. Nevertheless, their excellent conductivity is offset by the cost. Cheaper metal, such as copper, could be also used; however, its applications toward electrochemical electrodes are limited due to its oxidation and potential windows as discussed earlier. In air/oxidizing surroundings, copper or aluminum inks also provide poor conductivity owing to their surface passivation. This blocking surface shields particle-to-particle contacts. Thus, carbon-based materials such as graphene, CNTs, and graphite are among the most frequently used for compliant printed electrodes.[86,87] One grand obstacle of screen-printing technique is the use of binders in the ink, making it a challenge to eliminate the binder or surfactant stabilizers of the inks from the screen-printed traces. A potential solution is to eliminate the use of binder, although binder-free inks provide weak adhesion with the substrate, which introduces another critical challenge, particularly in flexible and stretchable electrodes that require mechanical robustness. Therefore, typically, the use of binder and stabilizers can only be reduced, not eliminated. Another approach is to decrease electrical junctions in the microscopic level of the printed electrode. The size of conductive fillers should be large, while the fillers need to be sufficiently small to form homogeneous composites. Graphene is an example. A strategy is demonstrated by preparing graphene platelet-based ink with a flake diameter of ~19 μm and a low content of polymer binder (less than 1% in weight) (Fig. 4e).[84] The printed graphene electrode provided good flexibility (even after repeated 1000 interactions of bending) and high conductivity of 8.81 × 10^4 S m^{-1}. This case represented versatility to fabricate the electrode on flexible substrates, such as PET and paper. Printed graphene oxide-based electrodes could be modified with protein-specific antibodies for various biosensors, such as influenza (Fig. 4f).[85]

Screen printing on porous fabric substrates causes another obstacle due to the presence of cracking and deformable structures. Hence, ink penetration in the fabric structure is crucial. Mechanically and electrically robust printed conductive traces on rough textiles could be realized by adjusting the ink's solvent. A low vapor pressure and boiling point solvent, such as carbitol acetate, could help the ink to deeply flow and anchor into the textile.[88] This

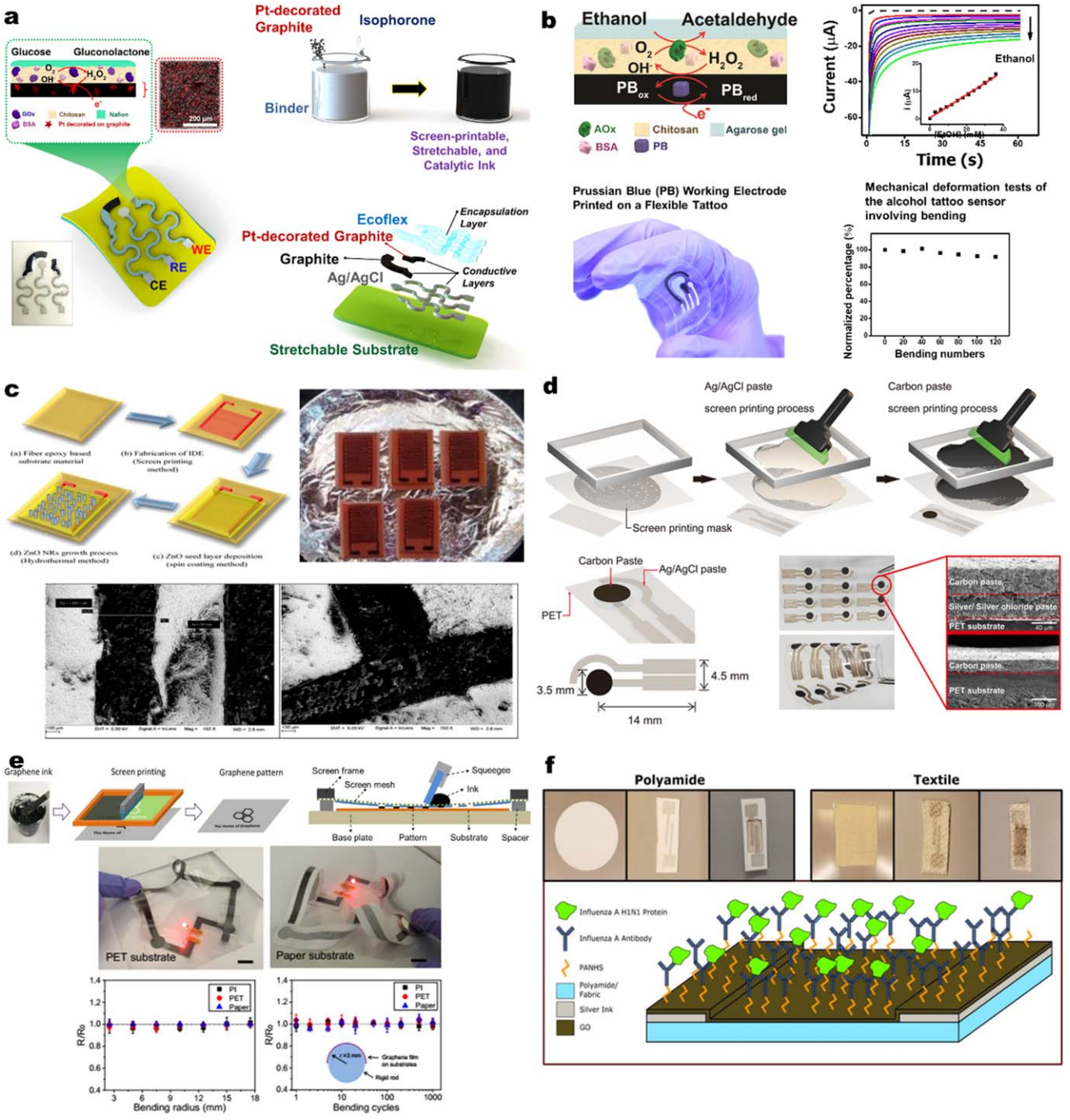

Figure 4. Examples of applications utilizing the screen-printing approach for flexible and stretchable electrodes. (a) Stretchable and screen-printed electrochemical glucose sensors. Adapted with permission,[7] Copyright 2017, Elsevier. (b) Flexible Prussian Blue-based electrode for ethanol sensors. Adapted with permission,[75] Copyright 2019, American Chemical Society. (c) Screen-printed interdigitated electrodes with zinc oxide (ZnO) nanorods for pH sensors. Adapted under the terms and conditions of the CC-BY,[79] Copyright 2019, Kumar et al., published by J. Electrochem. Soc. (d) Flexible polyaniline nanofiber-based arrays for pH sensors. Adapted under the terms and conditions of the CC-BY,[81] Copyright 2019, Park et al., published by Nano Converg. (e) Screen-printable graphene nanoplatelets inks for flexible electrodes. Adapted with permission,[84] Copyright 2019, American Chemical Society. (f) Screen-printed graphene oxide textile biosensor for influenza sensors. Adapted under the terms and conditions of the CC-BY,[85] Copyright 2018, Kinnamon et al., published by J. Electrochem. Soc.

strategy allowed high stretchability (up to 450%) and good resistance (0.06 Ω sq^{-1}).

Screen printing technique could be combined with the transferring method. For example, AgNW ink was patterned on the rigid glass substrate.[89] The conductive traces were transferred on low-modulus PDMS. Oxygen plasma was also beneficial to enhance the wettability of these electrochemical sensors,[89] offering a compliant printed electrode array for the battery-free and wireless electrochemical system. Note that oxygen plasma could also generate functional groups on electrodes for enhancing electrochemical sensing functions.[90]

Limitations of inkjet-printing approaches.—The inkjet-printing technique, based on the contact-less deposition, is another patterning

strategy. This route eliminates the requirement of stencils or masks for the fabrication of mechanically compliant electrodes on flexible and stretchable substrates.[91,92] Compared to lithography, inkjet printing is low cost and less complicated; moreover, this approach can reach a benign resolution of a few μm. This approach is used to fabricate various electrode materials, such as gold,[93–95] platinum,[96] and silver.[97–99] Although inkjet printing represents excellent capabilities for flexible and stretchable electronics, many challenging parameters must be considered, such as printing multilayers to allow desirable thickness and conductivity, inks sintering, surface treatment, cartridge specifications, and many detailed printing process parameters. To ensure good fluid flow, one important parameter is the size of ink particles to guarantee stable jetting and minimize nozzle clogging. In addition, like the screen-printing approach, the removal of organic surfactants from the surface of the inkjet nanoparticles is crucial to maximize the conductivity or control the morphology of mechanically compliant electrodes. An example of such utilization of the sintering process to engineer the surface of the electrode is the induction of particles to agglomerate, generating large clusters and porous structures useful for sensing purposes.[96]

Inkjet and transfer printing approaches could be synergized for the fabrication of flexible CNT electrodes, e.g., for electrochemical dopamine sensors.[100] With this route, CNTs could be patterned on a PDMS underlying substrate. One challenge is to achieve good conductivity because a single layer provides poor electrical conductivity. Each step of inkjet printing could create only a thin layer (e.g., ~0.1 μm). Therefore, it is essential to print multiple times. The increase in processing time offsets the advantage of inkjet printing, representing another challenge for fast manufacturing processes. Ten printed layers showed sheet resistance as high as 15 MΩ sq^{-1}. In order to drop the electrode resistance to be in a range of ~910 kΩ sq^{-1}, it needed 50 repeated printing times. The affinity between CNTs and the single-stranded DNA also allowed the fabrication of aptamer-based sensors, e.g., for lysozyme detection[101] (Fig. 5a).

Inkjet printing allows for the capabilities to print microelectrode arrays. For example, the nanoporous carbon microelectrode, with a high resolution electrode pitch of 30 μm, was demonstrated.[106] The inkjet printing process allowed different printable materials, including silver nanoparticles, nanoporous carbon, and a polyimide passivation insulative layer. The underlying silver trace was printed to ensure high conductivity. Graphene is another example of a materials commonly used for flexible electrochemical sensors. Graphene circuits could be deposited on the polymeric film substrate by transferring the graphene pattern, which was printed on rigid or flexible supports.[107] The inkjet printing could pattern graphene electrodes with benign finger dimensions of 400 μm finger width and 250 μm finger-to-finger gab. This strategy allowed a sheet resistance of ~0.2 kΩ sq^{-1} with high mechanical stability (even bending the electrode for 100 iterations after 100 or washing for 24 h cycles). Recently, large-area flexible graphene thin film was also demonstrated by utilizing drop-on-demand inkjet printing technique.[108]

In addition to carbon materials, conducting polymers, such as poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), are attractive groups of electrode materials for electrochemical devices.[109] One challenge is the weak coating on the hydrophobic elastomer. A surfactant can help to adjust the hydrophilicity of aqueous suspension of PEDOT:PSS ink on a PDMS substrate and also to soften the resulting conductive film.[110] Triton X-plasticized PEDOT:PSS ink was demonstrated to fabricate inkjet-printed transparent polymeric thin films.[111] In addition, composites of conducting polymers and carbon and (such as graphene/polyaniline nanocomposites[112]) are of interest. The printed platform of conductive polymer-based electrodes offered flexible platforms for various electrochemical analysis, such as glucose sensing[102] (Fig. 5b).

Long-term stability of flexible and stretchable sensors is another challenge. An approach to address this issue is to roughen the surface of the electrode, thus improving the adhesion between the functionalized sensing layer and the underlying electrode. Inkjet printing of nanoparticle ink is an alternative route to satisfy such a requirement. Nanostructured platinum could be inkjet-printed on flexible substrates (as shown in Fig. 5c).[96] Water-based platinum ink represented a route, not only to create highly rough surfaces, but also to enable a curing temperature of 180 °C. The resulting resistance was 6.3 Ω sq^{-1} (1.58 $\times$ 10^6 S m^{-1}, 16% of bulk Pt) when cured at 180 °C for 30 min. The primary consideration in forming effective inks is the choice of dispersants. Copolymers with pigment-affine groups could be used to maximize the particle packing density and particle-particle contacting points in order to ensure good conductivity.

The passivation of metal particles causes another challenge. However, forming passivation can be applied for solid-state ion-selective electrodes. Instead of forming oxides, sulfide layers enable selective film for sensing applications. For example, Ag_2S could be induced to form on the inkjet-printed electrode, printed on a flexible and transparent PEN substrate (Fig. 5d).[103] This example allowed a flexible sulfide-selective sensor. Moreover, other metal oxides, such as CuO, could be printed to provide favorable electrocatalysis of biomolecules, facilitating direct biosensing (e.g., via glucose oxidation[104]) (Fig. 5e).

Another grand challenge of printed electrodes is fouling. An example is the application of flexible printed electrode for monitoring wound by detecting biomarker pyocyanin and uric acid. Inkjet-printed polyacrylamide-coated, CNT (PA/CNT) electrodes on a flexible PI substrate suggests the conformability to attach on wearer's wound (Fig. 5f).[105] Such a key component of PA cover printed on the sensing electrode possesses porosity (13 nm), minimizing passivating molecules (e.g., proteins and cellular biomaterials), thus allowing stable electrochemical functions in the artificial wound fluid. In addition, such inkjet-printed PA/CNT-modified electrodes have been used to detect antioxidants in complex matrixes.[113]

Limitations of photolithographic approaches.—Photolithography is used for patterning electrodes. In this approach, physical evaporation and deposition require metals or conductive materials to evaporate in order to be re-deposited onto the desired substrate. With photolithography, the resolution can reach ~70–90 nm size. The photolithography technology is developed for patterning on a substrate coupled with chemical etching (Figs. 6a–6b).[114,115] For the evaporating process, the adhesive layer between PDMS and the active layer (e.g., gold) requires titanium or chromium adhesive layers as an interlayer.[30,116] Gold thin films (<100 nm thick) on the PDMS can withstand uni-axial stretching to 100% strain. The stretchability of such gold films on PDMS relies on the percolation of the electrical pathway through a built-in network of gold ligaments and micro-cracks . During a stretching cycle, the elongation/compression of the substrate is taken up by the opening-closing of the micro-cracks between the gold ligaments and the tilt and twist of the gold out of the conductor plane, hence minimizing the strain on the metal film.[117,118] To improve stretchability, 3D micropattern structure can be applied to the surface of PDMS before gold deposition as shown in Fig. 6c.[41] However, in the photolithography process, a photoresist is required. Active material films on the PDMS surface may also crack during the drying of the solvent, and organic solvents may induce swelling of the elastomer PDMS substrate. In addition, when chemical etching is used, diffusion of corrosive chemicals into the porous PDMS matrix occurs, an undesirable effect for biodevices.

Traditional photolithographic schemes are not suitable for organic materials, such as PEDOT:PSS. Aqueous solutions involved in traditional photolithographic processes will damage acidic PEDOT:PSS films. For example, the widely used alkaline developer (tetramethylammonium hydroxide) for the positive photoresist does not easily form high-resolution patterns, since the acid PEDOT:PSS will decompose the positive photoresist. For the negative photoresist, the acidic component in the PEDOT:PSS will crosslink the resist, and the resist residual will be left on the unexposed areas.[122] PEDOT:PSS is stable in its development of propylene glycol monomethyl ether acetate; therefore, the epoxy-based negative photoresist (SU-8) was used to pattern PEDOT:PSS.[123] However,

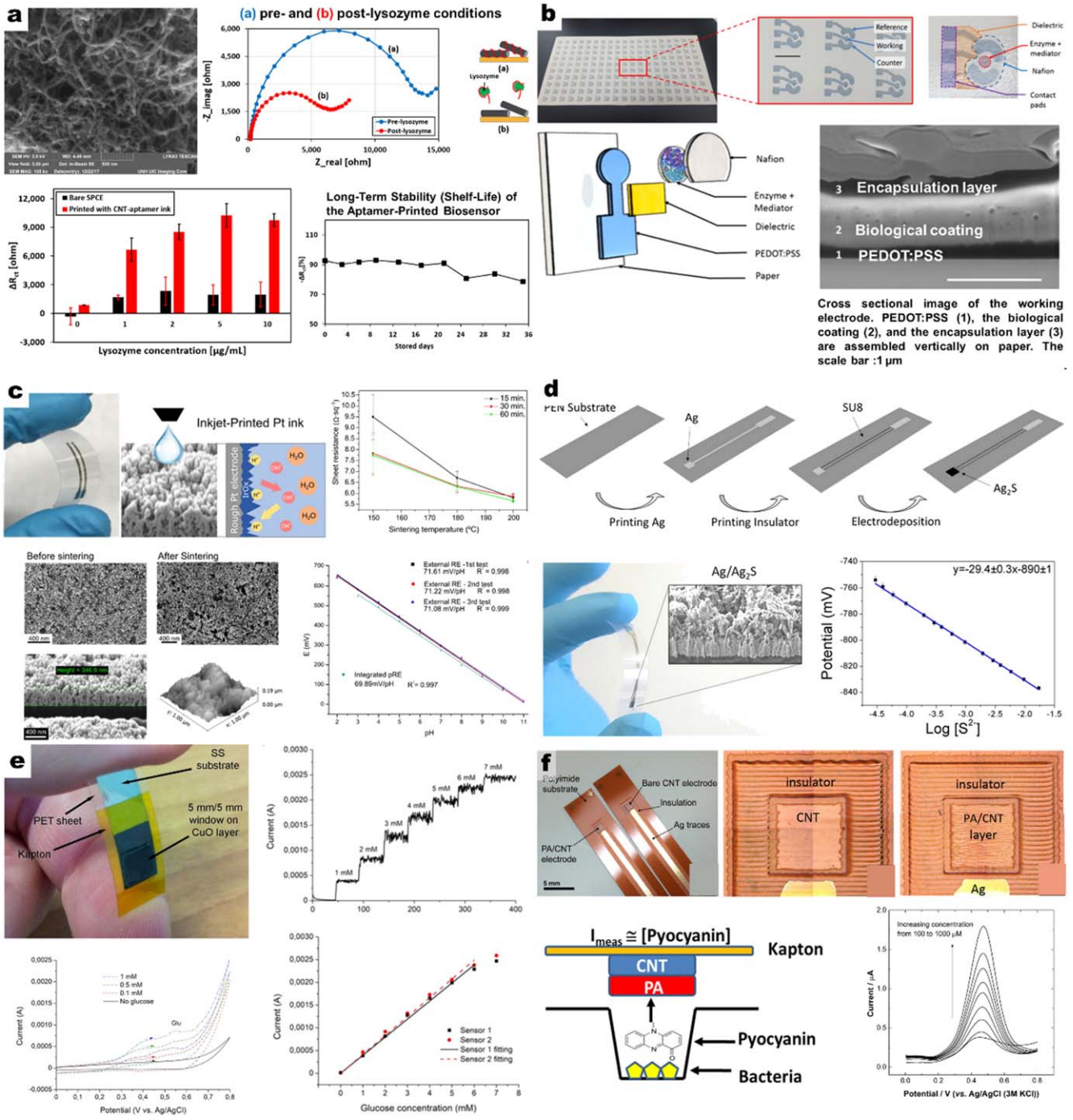

Figure 5. Examples of applications utilizing the inkjet-printing approach for flexible and stretchable electrodes. (a) Inkjet-printed aptamer-based electrochemical lysozyme. Adapted under the terms and conditions of the CC-BY,[101] Copyright 2018, Khan et al., published by Biosensors. (b) Inkjet-printed paper-based glucose sensors. Adapted under the terms and conditions of the CC-BY,[102] Copyright 2018, Bihar et al., published by npj Flexible Electronics. (c) Inkjet-printed rough platinum electrodes for stabilizing iridium oxide-based pH sensors. Adapted with permission,[96] Copyright 2019, American Chemical Society. (d) Inkjet-printed sulfide-selective electrodes. Adapted with permission,[103] Copyright 2017, American Chemical Society. (e) Inkjet-printed copper oxide-based electrodes for glucose sensors. Adapted under the terms and conditions of the CC-BY,[104] Copyright 2018, Bernasconi et al., published by J. Electrochem. Soc. (f) Inkjet-printed CNT electrodes for detecting pyocyanin and uric acid. Adapted with permission,[105] Copyright 2019, American Chemical Society.

SU-8 photoresist can hardly be removed after cross-linking, which limits its application. Additionally, the conductivity of PEDOT:PSS will decrease after the patterning processes. A strategy to protect PEDOT:PSS surface, such as using parylene, silver, or copper, is needed. However, the parylene film needs to be peeled off from the PEDOT:PSS surface, which is inconvenient for large-scale fabrication; moreover, residuals might exist on the PEDOT:PSS surface after the peeling-off process.[124] The removal of the metal protective layer, i.e., copper or silver, seems to be easier when compared to a parylene protector. The wet etch can be applied without the layer of PEDOT:PSS.[122,125]

Very stable materials (such as carbon, commonly used in electrochemical devices) are difficult to evaporate or etch; consequently, additional steps must be implemented. For example, graphene layer was first synthesized by chemical vapor deposition; subsequently, it was transferred to a PET sheet. The stable SU-8

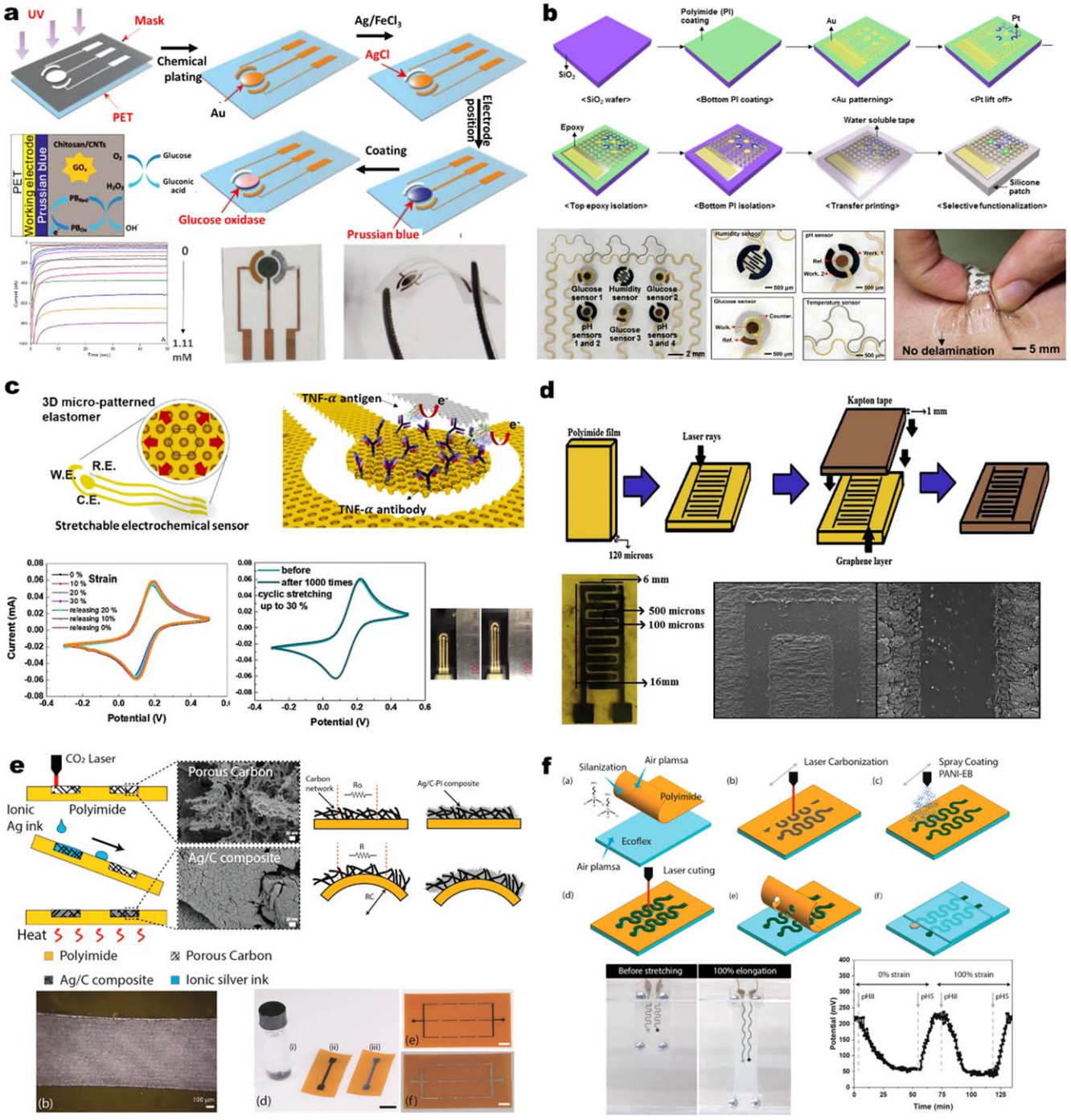

Figure 6. Examples of applications utilizing the photolithography and laser-assisted patterning approaches for flexible and stretchable electrodes. (a) Electrochemical sensors on the PET substrate for detection of glucose. Adapted with permission,[114] Copyright 2019, Elsevier. (b) Wearable/disposable glucose, pH, humidity, and temperature monitoring devices. Adapted under the terms and conditions of the CC-BY-NC,[115] Copyright 2017, Lee et al., published by Sci. Adv. (c) Stretchable electrochemical immunosensors, fabricated on 3D micro-patterned elastomeric substrate. Adapted with permission,[41] Copyright 2019, Elsevier. (d) Flexible graphene sensors for taste sensing applications. Adapted with permission,[119] Copyright 2018, Elsevier. (e) Femtosecond laser micromachining of a PI film coated with Au/Cr films for flexible sensors. Adapted with permission,[120] Copyright 2016, American Chemical Society. (f) Laser carbonization for stretchable potentiometric pH sensors. Adapted with permission,[121] Copyright 2017, American Chemical Society.

photoresist was applied to defined the active area of the electrode by photolithographic approach.[29]

Limitations of laser-assisted patterning approaches.—Laser-assisted patterning is another viable technique due to advantages such as the low cost of production, easy sample preparation, the ability to process a variety of raw materials, and usability for different functionalities (e.g., carboxylic acid functionalized multiwalled CNTs (MWCNTs)[126] and AgNWs.[127] It utilizes direct-patterning methods without molds or masks.[119] Different laser machines are available that can work precisely on samples via adjustable laser parameters. Hence, laser-assisted patterning techniques support the development of prototypes with a wide range of sizes and dimensions. For patterning electrodes, the active material was first formed on the substrate via dip coating, casting or spin-coating. The electrode was then designed by laser-patterning. Three important

laser parameters, power, speed, and *z*-axis, needed to be optimized during each patterning (Figs. 6d–6e).[119,120] The patterning resolution is limited to tens of micrometers.

Another approach of the laser is writing. This approach is based on a high-power laser beam that facilitates effective phase conversions of organic or inorganic materials on highly defined areas. Suitability for continuous processing makes this approach attractive formanufacturing flexible devices. Motivated by the unique advantages, laser processing has been used with graphene or polymers. For example, serpentine carbon traces can be directly carbonized from a PI sheet that is bonded to an elastomeric substrate by a powerful CO_2 laser.[38,128] Localized high temperatures and high pressures due to the energy from laser irradiation could easily break the C–O, C=O, and N–C bonds, which are rearranged to form porous structures.[129] The adhesive property of the induced film can increase by silanization to cover PI surface with organofunctional alkoxysilane molecules before being placed on an Ecoflex substrate treated by air-plasma (Fig. 6f).[121] Strong Si-O-Si covalent bonds between the PI backing of the electrode and the Ecoflex substrate can withstand elongations up to 135% and are robust for over 12,000 stretch-and-release cycles at 20% strain without a noticeable change in the electrical resistance.[38] Another example is employing the direct irradiation of the laser beam, focused onto a block copolymer thin-film coated on a graphene layer, successfully inducing self-assembled morphologies with controlled orientation of nanodomains such as vertical cylinders and lamellae.[130]

Meeting Challenges of Electrochemical Energy Sources for Powering Sensors

Apart from developing electrochemical sensing units, which mainly consist of electrodes, recognition layers, and underlying flexible/stretchable substrates, complete sensing systems also mandate viable and effective energy sources to power sensors.[131,132] Sensors meet major obstacles due to the limited lifetime of energy-source competencies of integrated energy-supplying devices. Considering the perspectives of real practice of sensors for biomedical applications that are typically applied for wearable and implantable purposes, power units must be miniaturized, light, and mechanically compliant.[133,134] This has significantly stimulated the research attempt to improve energy densities of energy-storage devices. Rigid lithium-ion batteries, without a self-charging strategy, are generally used for sensors. Flexible and stretchable electrochemical energy-storage devices, including supercapacitors and batteries, will be discussed in the section of flexible and stretchable energy-storage devices. To move forward to seamlessly and effectively innovate full sensing systems, properties that include small size, flexibility, and stretchability must be addressed. While developing these properties are primary challenges in the developing systems, long-term stability, functions, and reliability are also others key properties to be developed. Many conventional electronics for electrochemical sensors require a high-voltage battery supply. An example of energy-efficient electronics could be engineered to operate the biosensing system directly at 0.3 V.[135] Apart from only relying on energy-storage devices, another promising alternative to address such challenges is to leverage energy-harvesting devices that can extract the energy from surroundings for sustainable sensing operations.[136] Many energy-harvesting devices have been demonstrated, such as piezoelectric generators,[137] thermoelectric generators,[138] triboelectric generators,[139] and solar cells.[140] One of the most attractive strategies for biomedical sensors is to scavenge energy from human biofluids by utilizing biofuel cells (BFCs).

Flexible and stretchable biofuel cells (BFCs).—Employing BFCs as self-sustainable power sources that can convert biochemicals (such as glucose, lactate, and ascorbic acid) into electricity could resolve power issues in wearable or implantable systems.[135,141–143] However, scavenging energy from biomolecules for biomedical sensors still faces many challenges because BFCs need to enhance the electrical output to sustainably power sensors and maintain electrochemical functions under mechanical strain. Some detailed challenges, including enzyme-related aspects and effects of oxygen fluctuations, have been discussed.[144,145]

Recently, numerous efforts have been made to develop flexible and stretchable BFCs. Stepping forward from traditional rigid BFCs, stretchable glucose BFCs that could maintain the electrochemical functions even after being repeatedly stretched by 300% were demonstrated.[44] Moreover, stretchable textile-based fructose BFCs could be repeatedly strained by 50% with an output deterioration of 20%−30%.[146] Utilizing BFCs is an exciting route for fabricating compliant and autonomous biosensors to act as stand-alone sensing units.[147] Self-powered biosensors based on BFCs offer unique capabilities to build miniaturized, flexible, and stretchable biosensing systems. For instance, glucose and lactate BFCs were fabricated on a modified nylon/spandex substrate.[8] Such stretchable textile-based BFCs could sustainably drive the electrochemical biosensing unit, where the electrical output directly harvested only from sweat can indicate the level of the analyte (biofuel). This capability, together with mechanical robustness, allowed the on-body demonstration of the BFC-based sensor, representing a key progress in the advancement of self-sustainable biosensing systems that could open opportunities for new designs of conformal devices. Further developments have been demonstrated by integrating BFCs with epidermal microfluidic silicone devices, allowing development of soft and battery-free sensing systems.[148] Besides, an array of BFCs in series could be fabricated, offering a net voltage approaching 3.2 V (Fig. 7a).[149] This example also provided a linear increment between the generated power and the glucose level (1–25 mM), covering the expected value of urine glucose levels. This suggests opportunities for integrated self-powered biosensors.

Since fabric BFCs are interesting for convenient integrations, many yarn-based BFCs have been reported.[62,154] Recently, flexible enzyme/CNT fibers woven on the cotton textile were demonstrated.[155] The flexible anode and cathode fibers were prepared by coating MWCNT with glucose dehydrogenase (GDH) and bilirubin oxidase (BOD), respectively. The BFC yielded high power even when distorting the device at a wide range of temperatures (4 °C–50 °C). However, the fabrication of stretchable yarn-based BFCs holds extra critical challenges. An approach to add stretchability to the device is rewrapping MWCNT sheets on the rubber fiber.[156] The electrode base, which was the MWCNT sheet-wrapped rubber yarn, was functionalized and cross-linked with enzymes and mediators. Subsequently, such biocatalytic systems were re-trapped with MWCNT sheets, enhancing the BFC stability. The resulting BFC could retain the power performance even 100% stretching strain. Mechanically compliant BFCs can also be coupled with energy-storage modes,[150,157] which will be discussed further in the following section. An example is a stretchable BFC integrated with a supercapacitor on a textile substrate (Fig. 7b).[150] This combination represented an idea to maintain steady output and store the electrical output harvested by BFCs, potentially useful for integrating with all-in-one sensing systems.

A contact lens-based BFC represents another potential platform. However, the mechanical resiliency of the electrodes must be considered, as they should be flexible enough to conform on the spherical curvature. Flexible nanoporous gold electrodes on PET supports could be used for BFCs (Fig. 7c).[151] The porosity, which was generated by using dealloying protocols, is desirable to accommodate the immobilization of enzymes. This BFC could be used in artificial tear solutions, potentially expanding opportunities foradvances in self-powered biosensors (e.g., for lactate).

Flexible and stretchable energy-storage devices.—Supercapacitors—the energy storage devices bridging the gap between batteries and conventional capacitors—are candidates with safe operation, fast charging rates, long cycle life, and relatively simple configuration.[14,158] The electrochemical properties, mechanical integrity of the constitutive materials, and their assembly into

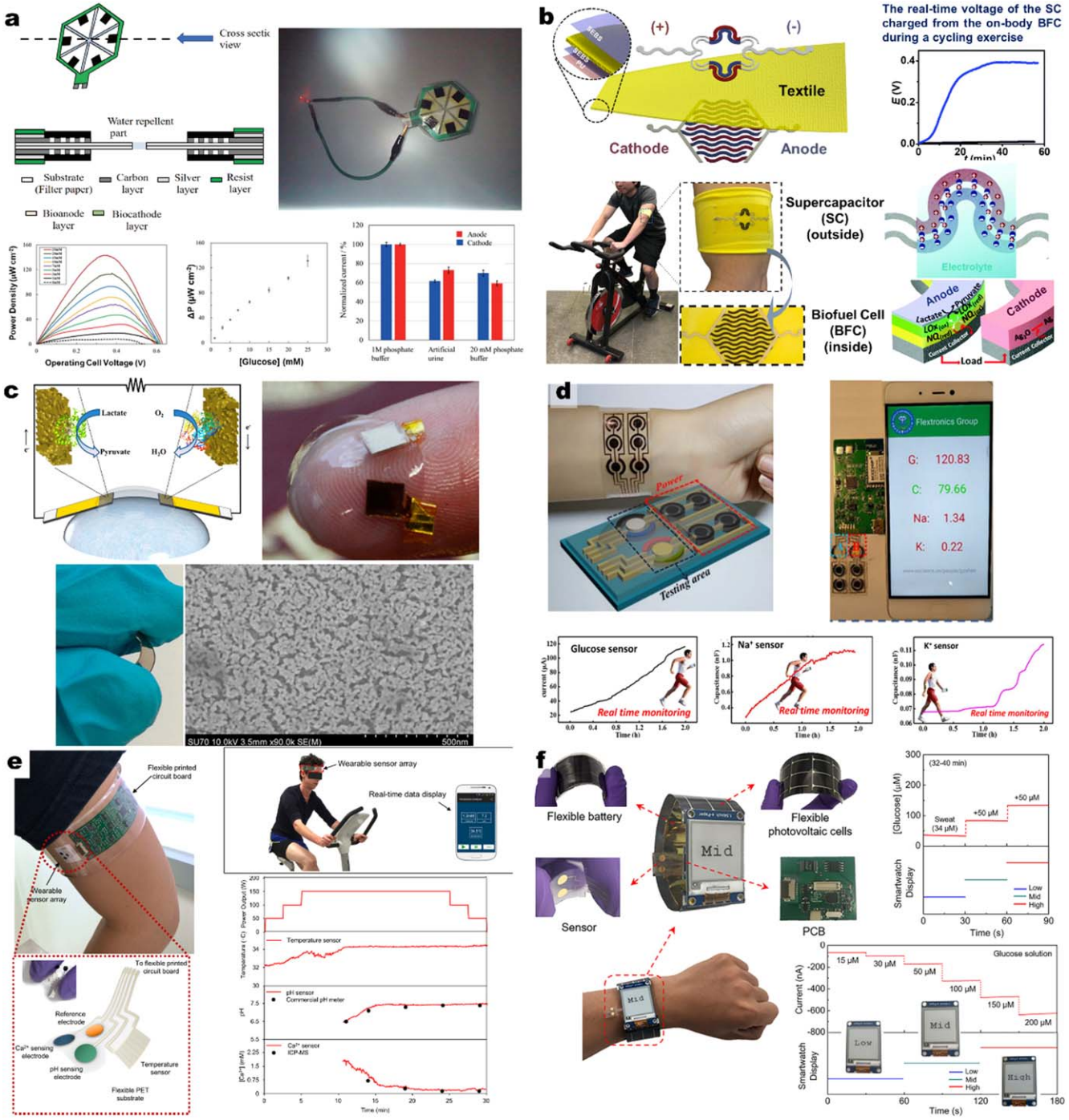

Figure 7. Examples of flexible and stretchable electrochemical power sources, including biofuel cells (BFCs), supercapacitors, and batteries. (a) paper-based self-powered glucose biosensor based on BFC array. Adapted under the terms and conditions of the CC-BY,[149] Copyright 2019, Shitanda et al., published by J. Electrochem. Soc. (b) Stretchable energy harvesting-storage hybrid textile devices, utilizing energy from sweat. Adapted with permission,[150] Copyright 2018, Royal Society of Chemistry. (c) Nanoporous gold-based BFCs on contact lenses. Adapted with permission,[151] Copyright 2018, American Chemical Society. (d) Wearable sweat monitoring systems with integrated microsupercapacitors. Adapted with permission,[57] Copyright 2019, Elsevier. (e) Wearable electrochemical platforms for noninvasive simultaneous monitoring of Ca^{2+} and pH. Adapted with permission,[152] Copyright 2016, American Chemical Society. (f) Self-powered devices for continuous sweat glucose monitoring. Adapted with permission,[153] Copyright 2019, American Chemical Society.

functional devices allow the integration of supercapacitors with compliant sensors. A major drawback that limits supercapacitor applicability in flexible and stretchable devices is the use of liquid electrolytes. The possible leakage of electrolytes is highly toxic and corrosive.[159] One strategy to resolve such issues is to develop all-solid-state supercapacitors, which have significant advantages in terms of flexibility and enabling applicable use in soft electronics when compared to liquid electrolytes.

Typically, flexible supercapacitors use sandwiched or in-plane interdigitated electrodes, consisting of thin-film electrodes, solid-state electrolyte, a separator, and a flexible packaging material.[159–161] Using solid-state electrolyte constitutes another challenge because it can significantly affect the rate capability and stability of supercapacitors. Gel polymer electrolytes are among the most common materials in solid-state supercapacitors as they provide relatively high ionic conductivity.[162] Carbon-composite

materials are widely used in flexible electrodes due to their outstanding electrical conductivity, cycling stability, power density, and mechanical properties.[163–165] Energy-storage devices built from MnO_2/CNT composites to store bioenergy harvested by the sweat-based BFC were introduced (Fig. 7b). The harvested bioenergy is stored directly and rapidly in the printed in-plane supercapacitors. The supercapacitor module showed high areal capacitance and cycling electrochemical stability.[150]

Foam-like structures with high porosity and robustness under mechanical stress are another formation for energy-storage devices. Composites of 3D graphene foams with a microporous network structure have received great attention because of the large surface area and excellent electrical and mechanical properties. It has a conductive graphene network, free of defects and inter-sheet junctions.[166] An example of this is a 3D porous foam formed from graphene and silver to produce a device capable of storing and releasing around three times more power than any similar flexible supercapacitor. Furthermore, the supercapacitor demonstrated high durability, showing that it provided power consistently across 25,000 charging and discharging cycles.[167] Usually, Ni foam is employed as the mold for 3D porous structure fabrication.[62,168] After obtaining 3D porous foam, Ni was etched away by using strong acid, introducing more complicated steps. Furthermore, the strong acid may oxidize the functional group of material, or may collapse the graphene network.[166]

Importantly, the flexibility, mechanical strength, and stability of energy devices rely on additional mechanical support. Current collector and capacitive electrode materials in a single fiber have been further developed. Free-standing $CuCo_2S_4$ nanosheets grown directly on a carbon fiber textile were prepared using one-step hydrothermal routes, and displayed remarkable performance as a flexible active electrode, exhibiting $3322\ F\ g^{-1}$ at $5\ A\ g^{-1}$ and excellent cycling stability with retention of 87% after 3000 cycles at $50\ A\ g^{-1}$ because of the absence of binder materials.[169]

Furthermore, microsupercapacitors are being considered since they offer higher performance than conventional supercapacitors due to their fast responses to ions and electrons. Microsupercapacitors received great attention due to their potential application in integrated flexible and stretchable sensors.[57,170] The developed concentric circular microsupercapacitor showed real application as an energy supply for a flexible sensor. When the microsupercapacitor arrays were connected in series and regulated by the voltage regulator, they served as the power source for real-time monitoring of glucose, Na^+, and K^+ in sweat (Fig. 7d).[57] The development of fabrication methods has enhanced capacitance and conductivity. Nevertheless, the fabrication of a flexible and high-performance composite cathode with high mass loading and good mechanical properties is still a challenge.

Additionally, batteries became an attractive candidate for a self-powered flexible and stretchable sensor because they provide high energy density, high output voltage, and long-term stability.[171] Most of the built-in batteries for flexible and stretchable devices are rigid, bulky, and require external charging or frequent replacement.[115,152,172,173] Therefore, it is essential to develop compliant and viable batteries. As shown in Fig. 7e, the wearable multiplexed sensing system on a subject's arm consists of two parts: an electrochemical sensing area and a flexible printed circuit board (including signal transduction, processing, and wireless transmission to a mobile phone).[152] The device still required external charging. As discussed, energy harvested from surroundings could be used as a self-sustainable alternative to power chemical sensors.[14] A step forward from a bulky printed circuit to a fully self-powered wearable sensing system has been shown. A self-powered and integrated smartwatch was fabricated for continuous monitoring of sweat glucose levels. The design has a watch strap consisting of flexible photovoltaic cells and rechargeable batteries, electrochemical glucose sensors, customized circuits, and display units integrated into a dialing platform[153] as shown in Fig. 7f. Instead of using lithium-ion batteriesthat rely on toxic materials that can adversely cause serious issues,[174,175] the Zn-MnO_2 batteries were used in this example. Such Zn-MnO_2 devices serve as intermediate energy-storage units and the utilization of aqueous electrolytes eliminated safety concerns, which is critical for biodevices. Without external charging facilities, the smartwatch could be self-sustainable with photovoltaic cells and flexible Zn-MnO_2 batteries as energy-storage devices. Such an example delivered a stable and autonomous capability with a high energy-storage capacity to support the continuous functionality of sensing systems.

Meeting Challenges of Electronics: Flexible and Stretchable Electronics for Potentiostats, Controllers, and Communication Units

Sensing units and energy sources alone are not the only issue; electronic components must also be addressed to control flexible and stretchable sensors. Typical functions of electronics include to bias the sensing units, enhance and process signals, and show the readable information to the user. Wireless technology is also important for the communication between biomedical sensors and the external receiver. Among many challenges in the area of electronic development,[176–178] fabricating flexible/stretchable circuit boards for electrochemical sensors, which is one of the most critical aspects, will be discussed. Figure 8 shows representative examples of the development in flexible and stretchable circuitry that have potentials to integrate with electrochemical sensing systems.

A primary consideration to realize flexible/stretchable circuitry is the conductive connection in essential circuits or electronic components, such as a radio frequency identification (RFID) tag or antenna for transmission and reception of wireless waves.[184,185] Bottlenecks due to the lack of flexible materials are among the most critical obstacles when integrating electronics onto soft substrates. One strategy is printing thin conductive tracks with engineered conductive inks. The developments of inks and processing techniques are expected to enhance further in electronics for a new genre of fully integrated soft electrochemical sensing research. Therefore, various materials, such as graphene,[186] silver,[99,180,187,179] and gold[188] inks have been developed for applications in flexible and stretchable electronics.

Potentiostats are among the most powerful tools for electrochemical sensors. Although miniaturized rigid electrochemical instruments, such as potentiostats, have been described,[189,190] flexible/stretchable platforms of such electronics are still limited. This is due to the cumbersome nature of manufacturing processes and materials, which typically rely on stiff microelectronic components or silicon technology. Flexible printed circuit boards have been applied for electrochemical sensing systems, such as amperometry,[75,191] potentiometry,[192] iontophoresis,[75] and wireless battery-free electronics.[148] For example, a flexible printed circuit board integrated with microcontroller, Bluetooth low energy (BLE), and analog-to-digital converters for squarewave voltammetric detection was demonstrated.[193] Recently, an example of the low-cost paper-based potentiostat was also described.[181] This fabrication leveraged piezo inkjet printing to construct conductive silver and dielectric traces (pin connections, insulation layers, and circuit tracks) to integrate with commercial off-the-shelf silicon electronics on a flexible paper. This example could perform cyclic voltammetry, representing an attractive platform for the development of fully integrated sensing systems. Moving forward to stretchable electronics for integrated electrochemical sensing systems, it will require further efforts. One grand challenge is ensuring the firm attachment between the conformal substrate and rigid electronic building blocks (e.g., resistor and silicon-based chips). The potential direction could be the applications of the "island-bridge" design attached on soft substrates[182,183,194,195] or intrinsically compliant materials[196] that would open up the new spectrum of stretchable and fully integrated sensing devices. This article only introduces some key concerns of electronics when integrating overall flexible and stretchable sensing systems. More comprehensive information, such as flexible, stretchable, and thin-film conductors, transistors, radio frequency

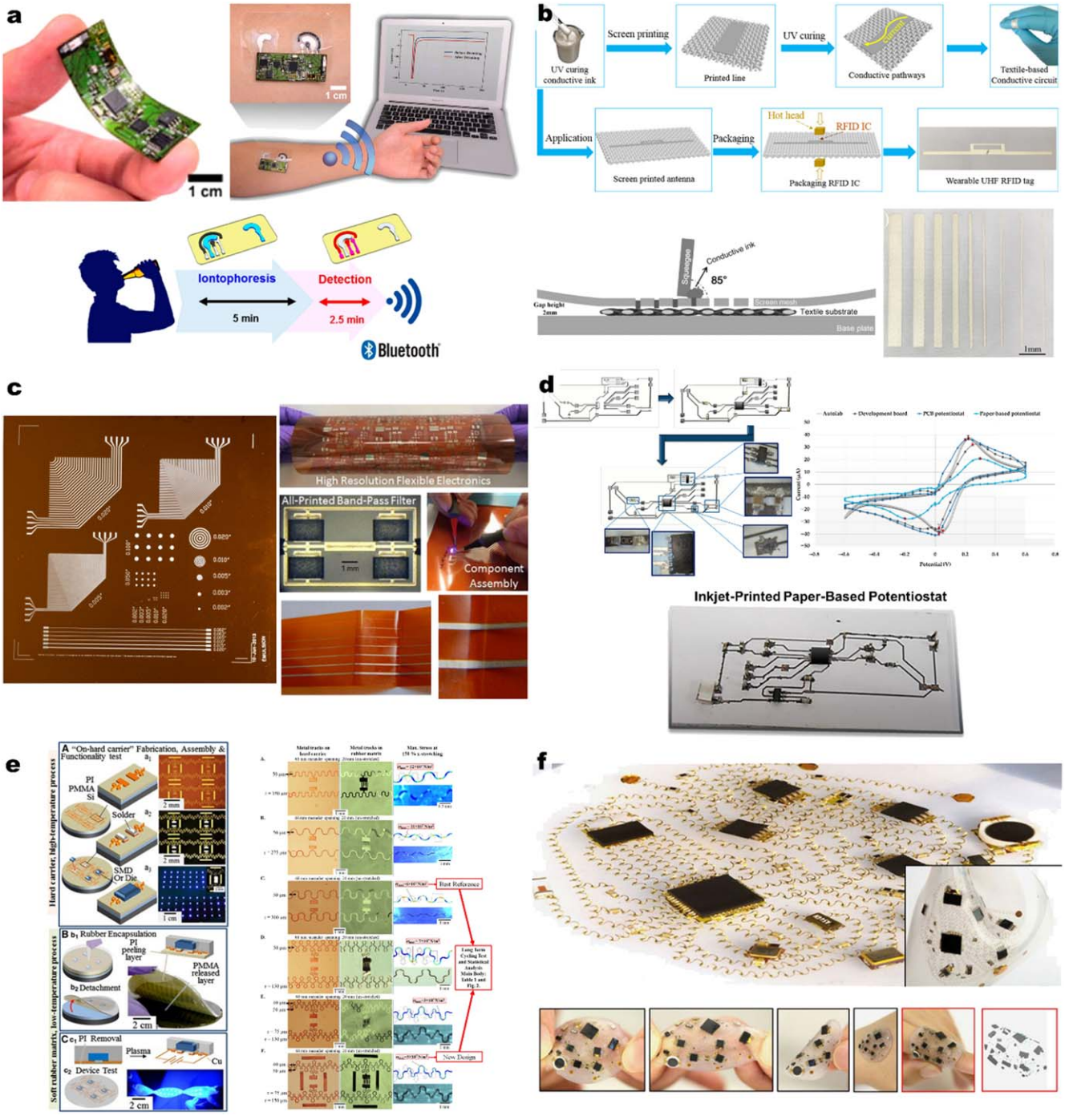

Figure 8. Possible solutions for integrated electronic-based challenges. (a) Flexible electronics for transdermal iontophoresis and amperometric detection. Adapted with permission,[75] Copyright 2016, American Chemical Society. (b) Textile-based circuits and wearable radio frequency identification (RFID) tags. Adapted with permission,[179] Copyright 2019, American Chemical Society. (c) Printed flexible electronics. Adapted with permission,[180] Copyright 2017, American Chemical Society. (d) paper-based potentiostats. Adapted under the terms and conditions of the CC-BY,[181] Copyright 2018, Bezuidenhout et al., published by Appl. Sci. (e) Deformable printed circuit boards. Adapted under the terms and conditions of the CC-BY,[182] Copyright 2016, Biswas et al., published by Npg Asia Mater. (f) Three-dimensional network designs for soft electronics. Adapted under the terms and conditions of the CC-BY,[183] Copyright 2017, Jang et al., published by Nat. Commun.

identification tags, electroluminescent components, etc, can be foundin earlier references.[197–201]

Futuristic Additional Features of Flexible and Stretchable Electrochemical Electrodes

Researchers aim to move existing conformal sensing systems toward broad applications. Hence, other characteristics of overall sensing devices should also be considered. Inevitable damage due to external strains and movement of the user may limit the durability of the integral device. Therefore, another primary feature such as self-repairing should be added into a new class of compliant electrodes.[202,203] The self-healing capability is vital to the durability of conventional electrode materials. However, as discussed earlier, when fabricating electrochemical sensors, materials for electrochemical interfaces should be judiciously taken into account. Figures 9a–9b

shows representative examples of developed flexible and stretchable self-healing electrodes that have the potential to integrate with electrochemical sensing systems. An example of magnetically self-healing electrochemical sensors was demonstrated.[204] The oriented magnetic particle/graphite composite was printed on a flexible polyurethane/polyester substrate, allowing self-healing via magnetic re-attraction after damage to the electrode. Carbon is also an outstanding material for electrochemical electrodes. Rucked graphene is another example that could be integrated with repairable elastomeric support.[205] The mechanism relies on reversible hydrogen bonding in the copolymer support. In addition to stretchability, such a self-healing graphene-based composite displayed a conductivity of 126 S cm^{-1} with the room-temperature self-healing feature. Moreover, polyampholyte gel electrolytes with reduced graphene oxide/biochar carbon electrodes, which also displayed self-repairable and stretchable properties, were also developed.[206] These examples suggest the capability to develop compliant electrode platforms for sensors and energy devices.[206,207]

Transparent characteristics of the electrochemical sensor represents another valuable virtue for flexible sensors since it provides the user privacy from unnecessary attention. More importantly, for in vivo purposes, an optical transparency is required to be integrated with the active electrode for the additional observation of biological tissues using simultaneous optical microscopy or modulation of ion imaging (Fig. 9c).[210,208] Transparent electrodes potentially allow the creation of new electrochemical platforms that can investigate signals using both light- and electricity-based modules.[211] Although indium tin oxide (ITO) is a dominant material for transparent electrodes,[212,213] the crystalline state and amorphous ITO have different properties. High transparency and low electrical resistivity are obtained from the crystalline state only. Hence, the transformation step form amorphous ITO to crystalline ITO is needed and is done by heat treatment at a temperature of at least 250 °C,[214] inappropriate for temperature sensitive substrate, e.g., soft plastics as discussed earlier in the underlying substrates section. In addition, the scarcity of ITO and its mechanical brittleness also raise issues. Alternatives have been widely explored in recent years, enabling efficient light delivery through electrodes and recording of electrophysiological signals concurrently with optical stimulation and imaging. Such devices are fabricated using optically transparent carbon-based materials (i.e., CNTs, graphene,[29,215–217]), conducting polymers,[218,219] and metal nanowires.[30,220–222] Although CNTs present good electrical, thermal, and mechanical characteristics, large contact resistance and extensive bundling of CNTs electrodes are observed. The electrode exhibits low electrical conductivity compared to ITO electrodes. Graphene is another candidate, but the large-area production of high-performance transparent graphene electrodes remains a serious issue. Although the chemical vapor deposition method has the ability of producing large-area graphene, it is offset by the high costs and extremely high temperature requirement.[223] Therefore, good conductivity, flexibility, and transparency of the sensing materials still needs to be developed. Metal

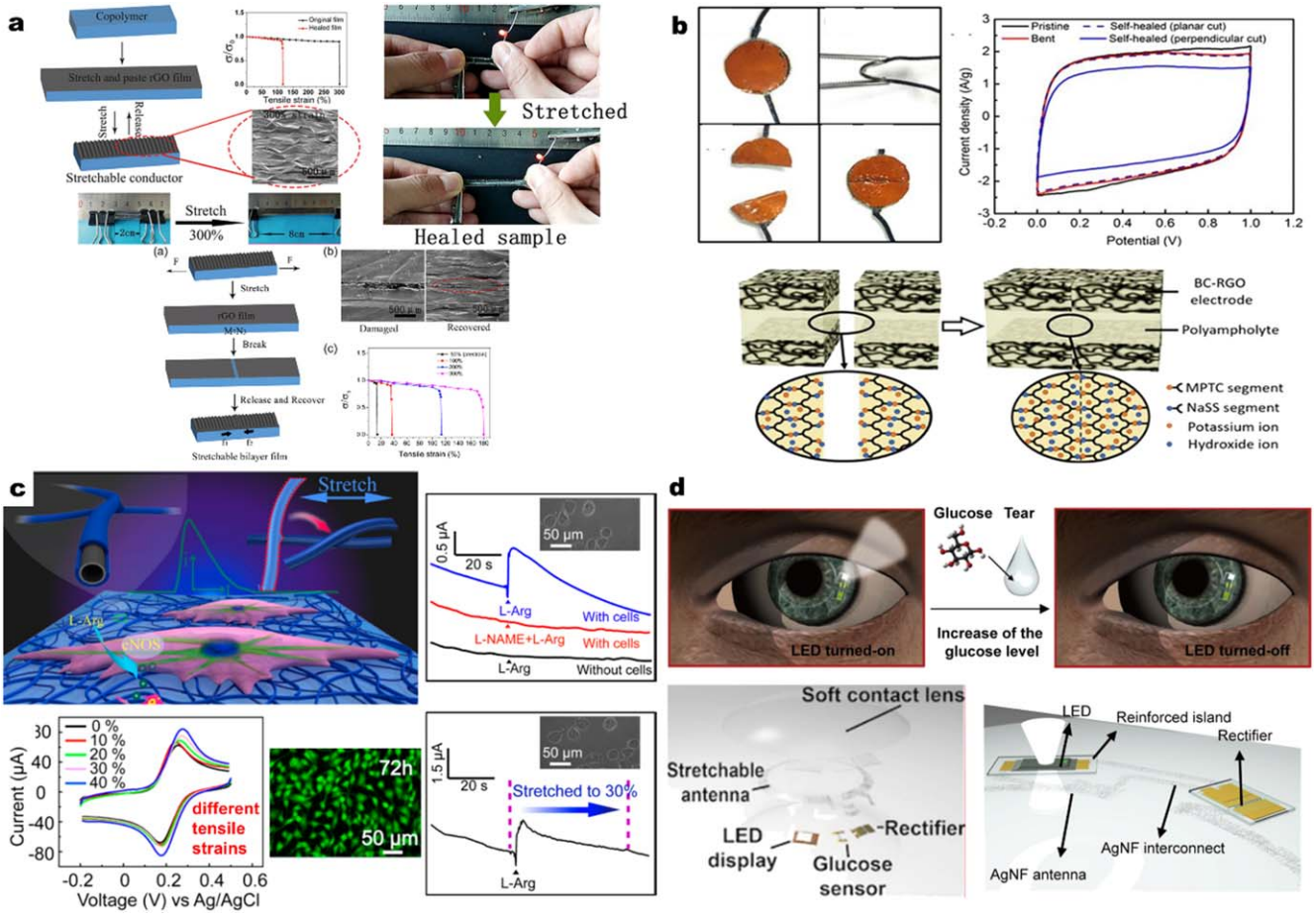

Figure 9. Examples of additional features, including self-healing and transparent electrodes, which have potentials to integrate with flexible and stretchable electrochemical electrodes. (a) Self-healing and stretchable graphene-based films. Adapted with permission,[205] Copyright 2019, American Chemical Society. (b) Self-healing and flexible supercapacitors. Adapted under the terms and conditions of the CC-BY,[206] Copyright 2017, Li et al., published by Sci. Rep. (c) Stretchable and transparent electrochemical sensor for real-time monitoring of mechanically induced biochemical signals from living cells and tissues. Adapted with permission,[208] Copyright 2017, American Chemical Society. (d) Soft contact lens for monitor glucose levels in tears. The soft contact lens is composed of a hybrid substrate, functional devices (rectifier, LED, and glucose sensor), and a transparent and stretchable conductor (for antenna and interconnects). Adapted under the terms and conditions of the CC-BY-NC,[209] Copyright 2018, Park et al., published by Sci. Adv.

nanowires are among the top candidate for a transparent and flexible sensor. As shown in Fig. 9d, a flexible contact lens for monitoring glucose levels in tears was developed. The sensor was fully integrated between the sensing part, wireless power transfer circuits, and display pixels to visualize sensing signals in real time, in which the increased glucose concentration in tear fluid changed the bias applied to the circuit. When the bias applied reached a threshold value, a light-emitting diode embedded in the device turned off.[209] At the moment, transparent electrochemical sensors are still being developed, representing an exciting research field.

Conclusions and Prospects

In this article, we took an overview of recent efforts to innovate integrated flexible and stretchable electrochemical sensing systems. Many researchers are exploring a variety of strategies to raise this promising technology to maturity. These include the development of mechanically compliant sensors, energy sources, and electronics. Such systems reinforce vital capabilities that fulfill and further advance the transformation from traditional sensors toward fully integrated electrochemical sensing systems. According to our analysis based on literature trends, it is expected that these emerging fields of new electrochemical sensing platforms are still continuously growing. We envision that innovative flexible and stretchable electrochemical sensing systems will yield a broad series of applications related to modern healthcare, consumer bioelectronics, and human–machine interfaces. Nevertheless, additional efforts are needed to expand modalities and functions, and many remaining challenges must be addressed to reach the next milestones in these research fields.

The primary challenge is to achieve electrodes with high mechanical stability, which mandate many approaches to address, as discussed in our review. Favorable functions, such as high sensitivity, fast response, low limits of detection, reproducibility, and/or multianalysis require substantial advances in materials and the production process. In some manners, especially biosensing applications where the detections are carried out in a complexes matrix, enzymes, DNA, or proteins are employed to ensure the selective detection. For example, if the electrochemical sensor is needed for in vivo examination, especially for humans, even more critical challenges would be considered. Inherent characteristics of biological systems, such as stretchability and dynamic manner, produce grand challenges. Robust adhesion between flexible and stretchable sensors is vital to ensure high signal-to-noise performance. This becomes particularly challenging when applied to wet environments, such as biological systems containing sweat and various biofluids. Adhesive layers must be engineered with the property of reversible adhesion in order to integrate with electrochemical sensing systems. Moreover, overall components in entire sensing systems should be biocompatible. It is important to ensure there is no toxic material, especially when applying the sensing system for in vivo applications.

Challenges related to three main components to build full sensing systems should be taken into account. First, for sensing aspects, most strategies for antifouling involve modification of the electrode surface with a coating or film of a protective layer to impart fouling resistance. However, it is also challenging to achieve compatible interference-preventing and antibiofouling layers that are mechanically compliant. To ensure selective detection, electrochemical biosensors are functionalized with a specific receptor, e.g., an ionophore; this is an example key for successful ion-selective sensors. Second, sensors require viable energy-storage devices. It is also essential to ensure that these energy sources are flexible and stretchable. Energy-harvesting devices are emerging tools to convert surrounding energy (e.g., photo, mechanical, thermal) into electricity. BFCs open new capabilities to act as self-powered electrochemical sensors. It is expected that this emerging field of energy-device research will help to expand the spectrum of miniaturized and conformal biosensors and bioelectronics in biomedical applications. Third, in parallel, flexible and stretchable electronics are of significance in diverse electrochemical applications, ranging from controlling the device to wirelessly signaling the data. In addition to design flexible and stretchable electronic components, the electronic circuitry should be carefully engineered to consume little power while still providing high performance. More thought-provoking research questions should be kept in mind. Ultimately, the technology of mechanically compliant sensing systems coupled with smart electronics is moving forward to integrate with the modern internet of things (IoT) and information and communications technology, particularly contemporary personalized healthcare management. Overall, many researchers anticipate realizing full comprehensive networks, big databases, and smart capabilities for real-time monitoring of all-inclusive information of physical and chemical data, early diagnosis, warnings, and therapeutic feedback.

Additionally, high-throughput and economical fabrications are important for realizing practical application of flexible and stretchable electrochemical sensing systems. Active materials are synthesized by sophisticated processes, and their high cost of preparation may cause a bottleneck. Simple strategies become the key to overcome such practical obstacles. Therefore, engineering materials and devices or improving fabrication processes are grand challenges, representing critical research questions. Moreover, ingenious state-of-the-art designs with extra functionalities, such as transparency of electrodes, can merge healthcare, biomedical applications, and the user's privacy, confidence, and fashion together.

Many aspects from experts in diverse research areas should be combined to generate new ideas and overcome remaining critical challenges. Due to continuing technical and material revolutions for conformal electrochemical sensors along with their integrated units (i.e., electronics and energy sources), this relevant field is shifting toward a variety of new applications, ranging from exciting studies in laboratory, soft robots, wearables, and implantables. Currently, commercialization efforts are also noticed. Some prototypes of flexible and stretchable electronics, such as wearable sensors for monitoring physical parameters, can be seen in the market; however, additional efforts are still needed to further develop electrochemical devices for bio-/chemical sensors. We expect that many exciting opportunities and breakthroughs still await and will be discovered soon.

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