Contents lists available at ScienceDirect

# Nano Energy

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

# Air-permeable electrode for highly sensitive and noninvasive glucose monitoring enabled by graphene fiber fabrics

Shengying Cai<sup>a,b</sup>, Changshun Xu<sup>b</sup>, Danfeng Jiang<sup>b</sup>, Meiling Yuan<sup>b</sup>, Qingwen Zhang<sup>b,\*</sup>, Zhaoling Li<sup>c,\*</sup>, Yi Wang<sup>a,b,d,\*\*</sup>

<sup>a</sup> School of Biomedical Engineering, School of Ophthalmology and Optometry, Eye Hospital, Wenzhou Medical University, Wenzhou 325001, PR China

<sup>b</sup> Engineering Research Center of Clinical Functional Materials and Diagnosis & Treatment Devices of Zhejiang Province, Wenzhou Institute, University of Chinese

Academy of Sciences, Wenzhou 325001, PR China

<sup>c</sup> Key Laboratory of Textile Science and Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, PR China

<sup>d</sup> Oujiang Laboratory (Zhejiang Lab for Regenerative Medicine, Vision and Brain Health), Wenzhou 325001, PR China

#### ARTICLE INFO

Keywords: Noninvasive glucose monitoring Wearable devices Textile electrode Graphene fiber fabric

# ABSTRACT

Developing wearable and noninvasive electrochemical devices for glucose monitoring is desirable for diabetes diagnostics and management. However, the adoptions are restricted by their poor reliability due to diluted glucose densities in commonly-used body fluids while lack of highly sensitive electrodes. Graphene fiber fabric, which is macroscopically paper-like and assembled by wet-fused graphene fibers, provides excellent electrical and mechanical properties as well as penetration paths for liquids, showing great potentials for electrochemical monitoring. Additionally, the graphene fiber fabric as a sensing patch provides excellent air-permeability which is necessary for wearing comfort but has rarely been addressed. As a result, the Prussian blue-decorated graphene fiber fabric exhibits a high electrochemical sensitivity to hydrogen peroxide (7298.7  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup>). After being modified by glucose oxidase and chitosan, it delivers both high selectivity and electrochemical sensitivity to glucose (1539.53  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 2–220  $\mu$ M, and 948.48  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 220-650 µM). We ascribe these performances to high-speed transfer paths for electrons and electrolytes in resultant electrodes. Additionally, the spontaneous absorption of body liquids by graphene fiber fabric after deposition of hydrophilic Prussian blue improves the utilization of active materials. Finally, the graphene fiber fabric used as a dry sensing patch was applied on human skin for the in vivo noninvasive glucose monitoring with the reverse iontophoresis (RI) technology, which showed good correlation to glucose levels measured by a commercial finger-prick glucometer.

# 1. Introduction

Increasing demands for personalized fitness monitoring have been attracting research efforts on the development of various noninvasive devices for metabolites analysis and medical diagnosis [1–6]. Among various bioelectronics, the noninvasive glucose monitoring device has drawn considerable attentions for its potentials in diabetes management, because commercially available glucometers always rely on invasive approaches that inevitably bring inconvenience and risk of bacterial infections [7,8]. In spite of numerous strategies have been developed for glucose detection, such as the measurement based on

metabolic heat, impedance, and polarization changes, it remains a big challenge to detect glucose with both high selectivity and sensitivity in noninvasive ways [9–14]. Direct measurements of glucose in body fluids through specific redox reactions seems to be a more promising solution [1,15–20]. One of the major challenges is the much lower glucose density in commonly-used body fluids for noninvasive tests ( $8 \times 10^{-3}$ –5 mM in sweat, saliva and tears) [21]. Although the glucose in interstitial fluid (ISF) has much higher concentrations (1.99–22.2 mM), it goes through substantial dilution during the reverse iontophoresis (RI) when indiscriminately and variably across a relatively large area of skin [22]. The concentration of the ISF glucose extracted via RI is approximately

https://doi.org/10.1016/j.nanoen.2021.106904

Received 29 October 2021; Received in revised form 11 December 2021; Accepted 27 December 2021 Available online 29 December 2021 2211-2855/© 2021 Elsevier Ltd. All rights reserved.







<sup>\*</sup> Corresponding authors.

<sup>\*\*</sup> Corresponding author at: School of Biomedical Engineering, School of Ophthalmology and Optometry, Eye Hospital, Wenzhou Medical University, Wenzhou 325001, PR China.

E-mail addresses: zhangqw@wiucas.ac.cn (Q. Zhang), zli@dhu.edu.cn (Z. Li), wangyi@wiucas.ac.cn (Y. Wang).

two orders lower than that of the corresponding ISF glucose level ( $\sim$ 19.9–222  $\mu$ M) [23,24]. Therefore, it is necessary to develop electrodes that produce large response current with diluted glucose in body fluids.

So far, electrodes for glucose monitoring, especially that use the slurry or ink as precursors, are usually constituted by compositing active materials (Pt, Au, Ag nanoparticles, NiO, CuO, Cu<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, Ni (OH)<sub>2</sub>, and/or Prussian blue etc.), with conductive agents (graphite, graphene, carbon nanotubes, etc.) and polymer binders (polytetra-fluoroethylene, polyvinyl, and Nafion, etc.) [24–29]. In this condition, insulating polymer binders will hinder the electron transport and result in poor electrical conductivity. Meanwhile their dense structure will block the electrolyte transport, leading to inadequate number of active sites. Besides of above-mentioned issues, a thin hydrogel layer (agarose

or polyvinyl alcohol) is typically applied on the electrodes to load enzymes, collect body fluids and improve the contacts between the electrode and skin during the extraction of ISF with the RI technology [15, 22]. Such a hydrogel film may further dilute the glucose, elongate the mass transfer paths and hinder the electron transfer due to the poor conductivity. In addition, the hydrogel layer as well as other electrodes based on conducting polyaniline, polythiophene derivatives, and reduced graphene oxide [30–32], lack efficient gas permeability, that prevent evaporation of sweat and emission of volatile organic components from human skin, causing skin irritation and reducing the comfort of wearing [33–37].

An efficient way to overcome these obstacles is to develop airpermeable electrodes with high-speed transfer paths for electrons, electrolytes and target molecules, as well as a 3-dimensional structure to



**Fig. 1.** Graphene fiber fabric-based sensing electrode for noninvasive glucose detection. (a) A schematic illustration for the preparation of the electrode, including (i) wet-spinning of graphene oxide fibers (GOFs), (ii) filtration of GOFs to graphene oxide fiber fabric (GOFF), (iii) converting GOFF to graphene fiber fabric (GFF) and (iv) electrodeposition of Prussian blue (PB) on GFF. (b) Optical photographs of the (i) H-type cell used for air-permeable tests, in which the smog was generated by igniting a mixture of rosin, flour, and ammonium chloride, (ii) GFF-PB used as a separator between neighboring rooms of the device, (iii) smog penetrated through the GFF-PB, and (iv) intact GFF-PB after the air-permeable test. (c) The schematic illustration of glucose sensing patch integrated by (i) GFF-PB-GO<sub>x</sub>-CS working electrode, (ii) carbon counter electrode, (iii) Ag/AgCl reference electrode, (iv) iontophoretic anode, (v) Cu current collector and (vi) PET substrate.

directly load enzymes and body fluids [38]. Graphene's assemblies, which are obtained through the wet-processing of graphene oxide and chemical/high temperature reduction methods, can be used as self-standing electrodes with high electrical conductivity without the need of using polymer binders [39–42].

Here, we propose a textile electrode consisted of the graphene fiber fabric (GFF) and a transducer layer of Prussian blue (PB) for the noninvasive detection of ISF glucose with the RI technology. Such a material featured by randomness in the fibrous architecture is distinguished from knitted or woven fabrics which have an ordered architecture of fibers interlaced to one another (knitting, sewing or weaving), and is classified into non-woven fabrics. The GFF was assembled by cross-linking graphene oxide fibers (GOFs) via a wet-fusing approach and subsequent annealing treatment. The cross-linking was achieved by hydrogen bonding between solvated graphene oxide (GO) sheets across the interface of contacted and swollen GOFs that were dispersed in aqueous solvent (or a mixture of water and ethanol) [43]. Prussian blue was deposited by an electrochemical method. The mechanical stability of the resultant electrode was confirmed by measuring the resistance changes under different bending angles. The sensitivity of the GFF-PB for the detection of glucose was further investigated upon direct modification of glucose oxidase (GO<sub>x</sub>) and chitosan (CS) on the water-absorbent GFF-PB rather than in a hydrogel film. The sensor showed a high sensitivity of 1539.53  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> to glucose in the concentration range of 2–220  $\mu$ M (and 948.48  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 220-650 µM), which was higher than that of most previously reported enzymatic electrodes ( $< 300 \ \mu A \ mM^{-1} \ cm^{-2}$ ) [1,4,44–51]. Finally, with the combination of RI technology, the air-permeable GFF-PB-GOx-CS film was applied as the skin patch and working electrode on human skin for the in vivo noninvasive measurements of glucose. The results were synchronously compared with the blood glucose measured by the finger-stick glucometer.

#### 2. Results and discussion

By applying a wet-spinning technology of graphene oxide (GO) in an ammonium bicarbonate aqueous solution, GOFs were successfully assembled in the rotating bath (Fig. 1a, i). Considering that ammonium bicarbonate was easily removed by decomposing to ammonia and carbon dioxide after drying beyond 60  $^\circ\text{C},$  the cleaner GOFs were obtained compared with that coagulated by previously reported multivalent metal ions or ethyl acetate [41,43,52,53]. Graphene oxide fiber fabrics (GOFFs) were then obtained through the filtration and wet-fusion of GOFs in a mixture of water and ethanol (Fig. 1a, ii). After treated with a chemical reduction process and well-established high-temperature annealing, the GOFFs were converted to the flexible, light-weight and highly conductive GFFs (Fig. 1a, iii). The X-ray diffraction (XRD) spectra in Fig. S1 demonstrates that the (002) peak of graphene shifts from 10.89° to 26.43° when the GOFF is converted to GFF, indicating the decrease of d-spacing from 0.812 to 0.337 nm after removing oxygen-containing groups on the graphene oxide. The PB nanoparticles were then deposited on the GFF (Fig. 1a, iv) as a transducer layer to reduce polarization bias during tests. The reduction potential of H<sub>2</sub>O<sub>2</sub> produced by enzyme-catalyzed oxidation of glucose on PB is much closer to 0 V than that on GFF, thus interferences at higher or lower potentials can be reduced as well [4,54,55].

It is a common knowledge that air permeability is often a necessary feature of comfortable clothing for wearable devices, whereas it has rarely been addressed by previous reports [32]. Therefore, the air-permeability of our electrode was demonstrated by a custom-made H-type cell using a piece of GFF-PB as the separator (Fig. 1b (i and ii)). As a result, smog generated by igniting a mixture of rosin, flour, and ammonium chloride in the left cell successfully penetrated through the GFF-PB and diffused into the right cell (Fig. 1b, iii). Moreover, the GFF-PB film still stay intact after the tests as shown in Fig. 1b (iv), indicating that the air-permeability is achieved by the porous textile structure rather than breakages produced by the airflow. More details of the experiment can be found in Movie S1. After loading of  $GO_x$  and integration with the RI technology, this breathable and wearable electrode can be applied to extract ISF from volunteers' skin for the noninvasive glucose monitoring as shown in Fig. 1c.

The photographs, scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) mappings of prepared GOFF, GFF, and GFF decorated with PB (GFF-PB) are compared in Fig. 2a-c, respectively. There is no obvious difference on the appearance and microstructure between the GOFF and GFF except the color changes from dark brown (GOFF in Fig. 2a, i and ii) to silver gray (GFF in Fig. 2b, i and ii). The GFF-PB shows a deep blue color (Fig. 2c, i) due to the deposition of a transducer layer with rough surface which is composed of PB nanoparticles, indicated in the SEM images (Fig. 2c, ii and Fig. S2). The oxygen element is completely eliminated in GFF after removing oxygen-containing groups of GOFF by high-temperature annealing (Fig. 2a and b, iii). The iron elements from PB nanoparticles are evenly distributed in GFF-PB, indicating the homogenous distribution of PB nanoparticles on cross-linked GFs (Fig. 2c, iii). Fig. 2d (statistic results from Fig. S3a and b) demonstrated that the fiber diameter is slightly increased from 25.93 µm in GFF to 27.61 µm in GFF-PB after the deposition of PB nanoparticles on graphene fibers. Such a thin transducer layer (~1.68 µm) would avoid significant changes on the porous and textile structure in GFF-PB.

In addition, the Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were employed to study the GFF-PB. As shown in Fig. 2e, the peak located at 1581 cm<sup>-1</sup> is attributed to the G band of graphene, representing in-plane vibration of highly symmetrical sp<sup>2</sup> carbon hexagonal. Disordered defect-induced double-resonant Raman process (D band) is almost unobservable at around 1350 cm<sup>-1</sup>, suggesting negligible defects on graphene. The 2D peak located at 2722 cm<sup>-1</sup> is the D-peak overtone, which ensures momentum conservation by involving two phonons with opposite wave vectors, thus appeared without the presence of defects [56,57]. Additionally, the C=N stretching vibration is found at around 2155 cm<sup>-1</sup>, consisting with the Raman spectra of PB and its analogues as reported by other works [58]. As comparison, the Raman spectra of the GOFF and GFF show no vibration peak at around 2155 cm<sup>-1</sup>, due to the absence of PB.

The XPS survey of GFF-PB, GFF, and GOFF are displayed in Fig. S4ac, respectively. The O1s peak (525–540 eV) in the spectra of GFF and GFF-PB is almost disappeared compared with that of GOFF. It is consistent with negligible signals of C-O-C (286.3 eV), O-C=O (287.4 eV), and COOH/COOR (288.1 eV) in their C1s deconvolution curves (Fig. S4d-f) [59–61]. Signals of N1s and Fe2p are observed in the spectrum of GFF-PB. The high-resolution XPS spectrum of Fe2p is shown in Fig. 2f. The binding energies at 708.5 eV and 721.5 eV are assigned to  $2p_{3/2}$  and  $2p_{1/2}$  of Fe<sup>2+</sup>, respectively, and peaks at 709.4 eV and 723.1 eV are attributed to  $2p_{3/2}$  and  $2p_{1/2}$  of Fe<sup>3+</sup>, respectively. The satellite located at 712.4 eV is resulted from the transfer of electrons from -CN- to Fe [62]. All of these results indicate that the PB is successfully formed on GFF assembled by high-quality graphene nanosheets.

The linear sweep voltammetry (LSV) measurements of GOFF, GFF, and GFF-PB are shown in Fig. 3a, respectively (with the size of 0.5 cm  $\times$  0.25 cm for all samples). The electrical resistance of the GFF-PB is calculated to be 1.66  $\Omega$  according to the Ohm's law, which is slightly larger than that of GFF before the deposition of PB (1.25  $\Omega$ ). However, both of the GFF and GFF-PB exhibit the resistances 3 orders of magnitude lower as compared with the GOFF (2117.52  $\Omega$ ). Additionally, electrochemical impedance spectroscopy (EIS) was carried out to investigate the electrochemical behaviors of GFF and GFF-PB from 0.1 to 100 kHz in PBS solutions (pH = 7). The low frequency portion in Nyquist plot of GFF-PB is steeper to the real component axis as compared with that of GFF, indicating the faster diffusion of electrolytes (Fig. 3b). This phenomenon is ascribed to the improved water wettability of GFF-PB. As shown in Fig. 3c and d, a drop of water is easily absorbed into



**Fig. 2.** Material characterizations. (a) The photographs (i), SEM images (ii), and EDX mappings (iii) of GOFF, (b) GFF, and (c) GFF-PB. (d) Diameter distribution of graphene fibers before and after the deposition of PB nanoparticles. (e) The Raman spectra of GFF-PB, GFF, and GOFF. (f) The high-resolution XPS scan for the GFF-PB of Fe2p peak.

GOFF by the capillary force of hydrophilic GOFs, whereas the contact angle between water and GFF is around 148°, representing a hydrophobic interface of material. However, the water-absorbent property is recovered as for GFF-PB (Fig. 3e), due to the introduction of hydrophilic PB on GFs. The GFF-PB shows a strong water absorption capability up to 43.5 times of its own weight (Fig. 3f). The detailed experiments for the water absorption of the GFF-PB sheets can be found in Movie S2. This water-absorbent property distinguished from traditional electrodes is beneficial for improving the collection of ISF for further noninvasive glucose monitoring.

In the cyclic voltammetry (CV) scan, GFF and GFF-PB show significantly different curves (Fig. 3g). Owning to different redox states of iron atoms in the PB crystal, obvious redox peaks of iron elements are observed in the CV curve of GFF-PB. The PB was transformed into Prussian white (PW) upon reduction of iron (III) to iron (II) at 0.18 V, while PW containing only iron (II) turns to PB upon oxidation at 0.22 V [63]. In contrast, only capacitive behavior is found in the CV curve of bare GFF (inset in Fig. 3g), representing a simple adsorption-desorption process of electrolytes. Furthermore, the CV scans of GFF-PB at different scanning rates shows that both anodic peak current ( $I_{pc}$ ) have a typical linear relationship with the scanning rates (Fig. 3h), indicating a quasi-reversible surface-confined

electrochemical process for GFF-PB [64].

It is reported that the PB suffers from inherent instability in aqueous solutions during CV scans and is easily exfoliated from electrodes, which can be indicated by largely reduced redox peak intensity in CV cycles [4]. Such an instable property of PB on electrodes will significantly affect their redox reaction with H2O2, and generates unstable current response. The stability of GFF-PB was thus investigated by cycling CV scan for 50 cycles (Fig. 3i, j). As a result, the anodic peak retains 93.33% and 71.90% of its original current at the 10th and 50th cycle, respectively (Fig. 3k). The cathodic peak shows current retention of 95.73% and 78.96% under the same conditions. This performance is better than that of a reported PB electrode before introducing the protective layer of nickel hexacyanoferrate [4]. The relatively higher stability can be attributed to a strong interaction between PB nanoparticles and graphene sheets reported by others [65]. Besides, the resistance of a GFF-PB  $(0.5 \text{ cm} \times 1.0 \text{ cm})$  is nearly unchanged under different bending angles from 0 to 180° (Fig. 3l and S5), exhibiting an outstanding mechanical stability that is enabled by robust junctions between GFs.

Fig. 4a shows typical CV scans of GFF-PB in a PBS solution (pH = 7) containing 1 mM H<sub>2</sub>O<sub>2</sub>. The reduction current of H<sub>2</sub>O<sub>2</sub> occurs in the region of 0.1 to - 0.1 V (versus Ag/AgCl). As shown in Fig. 4b and S6, GFF-PB delivers a staircase and fast amperometric responses upon



**Fig. 3.** Electrochemical and mechanical performances. (a) The LSV scans of GOFF, GFF and GFF-PB at a scan rate of 10 mV s<sup>-1</sup>. (b) Nyquist plots and corresponding fitting curves of the GFF and GFF-PB measured in PBS solution (pH=7). (Inset) Equivalent circuit diagram of the fitting curves. (c-e) The contact angle tests for GOFF, GFF and GFF-PB, respectively. (f) The photographs of the GFF-PB upon the absorption of water with CuCl<sub>2</sub>. (g) The CV measurements of the GFF and GFF-PB in PBS solution (pH=7), at a scan rate of 10 mV s<sup>-1</sup>. (Inset) Enlarged CV curve of the GFF (Y-axis: current density /  $\mu$ A cm<sup>-2</sup>, X-axis: potential versus Ag/AgCl / V). (h) The CV curves of the GFF-PB measured in PBS solution (pH=7), with increasing scan rate from 10 to 100 mV s<sup>-1</sup>. (Inset) The dependence of peak currents on scanning rates (Y-axis: current density / mA cm<sup>-2</sup>, X-axis: scan rate / mV s<sup>-1</sup>). (i, j) The CV scans of the GFF-PB measured in PBS solution (pH=7) during 1–10 and 10–50 cycles, respectively, at a scan rate of 100 mV s<sup>-1</sup>. (k) The retention ratios of peak current intensity as a function of cycling numbers deduced from i and j. (l) The changes in the resistance of the GFF-PB under different bending angles.

increasing the concentration of  $H_2O_2$  solutions. The results show the linear detection range from 5 to 50  $\mu M$  with the sensitivity of 7298.7  $\mu A$   $mM^{-1}$  cm $^{-2}$  for the detection of  $H_2O_2$  (Fig. 4b, inset). This ultrahigh sensitivity is ascribed to the high-speed transfer paths for electrons and electrolytes in GFF-PB, as well as the efficient diffusion of  $H_2O_2$  in the

active materials due to the above-mentioned good water-absorbent property. The influences of the PB deposition time to the sensitivity of GFF-PB are compared in Fig. S7. As a result, negligible difference is found with the deposition time increasing from 5 s (Fig. 4b) to 15 s, 30 s, and 45 s (Fig. S7a-c). However, when the deposition time is further



**Fig. 4.** Sensitivity and selectivity of the electrode. (a) The CV curves of the GFF-PB measured in PBS solution (pH = 7) with 1 mM H<sub>2</sub>O<sub>2</sub>, at the scan rate from 10 to 100 mV s<sup>-1</sup>. (b) The amperometric *I*-*t* response of GFF-PB upon successive additions of H<sub>2</sub>O<sub>2</sub> (5  $\mu$ M per step) into PBS solution (pH = 7). (inset) The current response versus the H<sub>2</sub>O<sub>2</sub> concentrations (Y-axis: current density /  $\mu$ A cm<sup>-2</sup>, X-axis: density /  $\mu$ M). (c) The CV curves of the GFF-PB-GO<sub>x</sub>-CS in PBS solution (pH=7), at the scan rate from 10 to 100 mV s<sup>-1</sup>. (inset) The dependence of peak currents on scanning rates (Y-axis: current density / mA cm<sup>-2</sup>, X-axis: scan rate / mV s<sup>-1</sup>). (d) The amperometric *I*-*t* response of GFF-PB-GO<sub>x</sub>-CS measured in the glucose concentration range of 2–10  $\mu$ M. (e) The amperometric *I*-*t* response of GFF-PB-GO<sub>x</sub>-CS measured in the glucose concentration dependent current responses in the range of 2–20  $\mu$ M and 220–650  $\mu$ M, respectively. The blue area shows the concentration range of extracted ISF glucose (~19.9–222  $\mu$ M). (g) Magnified view of the blue area in f. (h) The electrochemical sensitivity (2–220  $\mu$ M) of the GFF-PB-GO<sub>x</sub>-CS for the detection of glucose as compared with previously reported electrodes. (i) The amperometric *I*-*t* result of the selective response to glucose (Glu) and other interference molecules, including NaCl, Fructose, ascorbic acid (AA), dopamine (DP), and lactic acid (LA). The PBS (pH = 7) solution was used as an electrolyte in this condition.

increased to 60 s (Fig. S7d), the H<sub>2</sub>O<sub>2</sub> sensitivity reduces to 5031.9  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup>, which may be resulted from elongated transfer paths of electrons by an over-grown PB layer. Additionally, as control, the rGOFF-PB in which the rGOFF is only treated by chemical reduction shows sluggish H<sub>2</sub>O<sub>2</sub> response (Fig. S8) mainly due to its poor conductivity and weak electrons transfers (Note that the electrical conductivity of rGOFF with the same size of GFF was measured to be 14.72  $\Omega$  as shown in Fig. S9, which is more than 10 times higher than GFF). The results indicate that the high-temperature annealing of GFF plays an important role on the fast *I-t* responses. After immobilization of GO<sub>x</sub> and CS on GFF-PB, the electrode was applied for the investigation of glucose responses at different concentrations of glucose. The enzymatic activity of GO<sub>x</sub> on GFF-PB was confirmed by Fig. S10, in which the addition of

GFF-PB-GO<sub>x</sub>-CS in HRP-ABTS-Glu solution showed blue color similar as that of a contrast sample mixed with the free GOx solution, indicating the generation of  $H_2O_2$  by the enzymatic reaction. The resultant enzymatic electrode shows a similar CV shape with that of GFF-PB (Fig. 4c), except for the wider redox peaks caused by extra paths for mass and electron transfer. As for glucose detection, the response current of GFF-PB-GO<sub>x</sub>-CS is generated by reduction of  $H_2O_2$  produced through enzyme-catalyzed oxidation of glucose on GFF-PB (Fig. 1c), thus the higher  $H_2O_2$  sensitivity for GFF-PB will pave a way for the better glucose sensitivity of GFF-PB-GO<sub>x</sub>-CS. As a result, the GFF-PB-GO<sub>x</sub>-CS shows a high glucose sensing sensitivity of 1539.53  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 220–650  $\mu$ M) (Fig. 4d-g). It is much higher (>

3.8–6.2 times) than that of other reported enzymatic electrodes (Fig. 4h) [1,4,44–51]. In addition, the amperometric I-t response of GFF-PB-GO<sub>x</sub>-CS and GFF-PB-GO<sub>x</sub> upon glucose reaction are compared in Fig. S11. The GFF-PB-GO<sub>x</sub>-CS shows a typical staircase drop in the *I-t* measurement, while only sluggish current decreases are observed for the GFF-PB-GO<sub>x</sub>. We attribute the faster response of GFF-PB-GO<sub>x</sub>-CS to the suppressed dissolution of GO<sub>x</sub> into PBS solution as protected by the CS, which ensures higher enzyme concentrations on the electrode. In this situation, the H<sub>2</sub>O<sub>2</sub> produced by enzyme-catalyzed oxidation of glucose on the surface of electrode can be reduced by PB directly with short transfer paths, generating fast electrical responses. Note that the spike current response appeared on the GFF-PB-GOx-CS electrode upon the addition of glucose could also be ascribed to the faster catalytic reaction on the GFF-PB-GOx-CS electrode, i.e., the whole reaction process is limited by mass transport (Fig. S11). While for the GFF-PB-GO<sub>x</sub>, the GO<sub>x</sub> without the immobilization of CS might be dissolved into the solution thus induce lower reaction rate than the mass transport of glucose and H<sub>2</sub>O<sub>2</sub> diffusing to/away from the electrode, i.e., the reaction process is limited by the catalytic reaction [66,67]. Furthermore, the selectivity of the sensor for the detection of glucose was investigated with other interferents such as sodium chloride, fructose, ascorbic acid, dopamine, and lactic acid. As a result, glucose exhibits the distinct current change whereas interferent molecules show a negligible current response, indicating the good selectivity of the sensor for the detection of glucose (Fig. 4i).

Further application of the textile enzymatic electrode on wearable monitoring of glucose was illustrated by integrating it with the RI technology on a screen-printed sensing patch attached on a volunteer's wrist (Fig. 5a and b). Prior to the measurement, the construction of the electrodes was optimized (Fig. S12a-f). In comparison with CV curves of the GFF-PB-GO<sub>x</sub>-CS fixed by a Pt holder (Fig. 4c and S13), integrating the electrode with the carbon current collector prepared by screen-printed method (Fig. S12a) shows weak and distorted redox peaks (at around 0.2 V, Fig. S12d). Alternatively, introducing Cu current collectors below carbon layers (Fig. S12b) significantly increased the electrochemical signals of the electrode (Fig. S12e). It should be noted that although direct integration of the GFF-PB-GO<sub>x</sub>-CS on Cu current collectors (Fig. S12c) produced the largest response signals (Fig. S12f), this strategy was abandoned due to the copper corrosion occurred during tests (inset in Fig. S12f).

As skin carries a net negative charge at physiological pH, the majority of current carriers through the skin are Na<sup>+</sup> ions, which produces a convective solvent flow and transports uncharged glucose towards the iontophoretic cathode [15]. Upon employing an iontophoretic voltage of -3.0 V on the sensing patch coupled with a printed carbon electrode as iontophoretic anode, ISF can be extracted from subcutaneous tissues and absorbed into the textile electrode. The subject underwent finger-prick blood sampling for glucose measurement by commercial glucometer at the time RI was about to applied on the skin (Fig. 5c). The current responses for the in vivo noninvasive monitoring of glucose were thus compared with the blood glucose levels measured by the finger-prick glucometer. The current responses recorded before and after RI are considered as the current changes (i.e.  $\Delta I = I_x - I_0$ ). For all electrochemical measurements, average values of the current in *I-t* curves at the t = 60,



Fig. 5. In vivo noninvasive measurements. (a) Images of the GFF-PB-based sensing patch on a volunteer's wrist. (b) Enlarged view of the sensor and iontophoretic anode in a. (c) In vivo invasive blood glucose measurement by using a finger-prick glucometer. (d) The amperometric I-t curves before and after RI recorded from the sensing patch attached to the skin surface during a 5-hour period. (e) Magnified view of the response current in d after RI at different pointin-time. (f) Results of glucose monitoring in 5hour period by using a finger-prick glucometer (red) and the GFF-PB-based sensing patch (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

70, 80, 90, 100 s are calculated as  $I_x$  (where x denotes the point-in-time during the period of in vivo tests). Fig. 5d and e provide *I*-t curves obtained by the volunteer during a 5-hour measurement before (x = 0 h) and after RI (x = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 h). As a result, the variation trend of  $\Delta I$  which represents the glucose density in ISF (blue squares) matched well with the glucometer results (red squares) (Fig. 5f and S14), in spite of a 20- to 30-min of time lag. This time-lag phenomenon is due to the 20- to 30-min intrinsic density delay between glucose in ISF and blood [3]. The current change  $\Delta I$  for in vivo tests on our sensing patch is about 0.1679  $\mu$ A (i.e. 0.1485  $\mu$ A cm<sup>-2</sup>) versus per mM blood glucose, which is better than or comparable to that of other reported analogous sensors [3,22,24]. In addition, the current changes can be further improved by optimization of RI parameters such as bias voltage and electro-osmotic time [68].

# 3. Conclusion

In conclusion, we have proposed an air-permeable electrode by deposition of PB nanoparticles as transducer on the GFF and applied for the wearable noninvasive monitoring of glucose in vivo on human skin. Benefiting from the robust connection between GFs cross-linked by a wet-fusing approach, the GFF-PB exhibits an outstanding mechanical property and retains its resistance at different bending states. After immobilization of GO<sub>x</sub> and CS, this electrode delivers a glucose sensitivity of  $1539.53 \,\mu \text{A} \,\text{m} \text{M}^{-1} \,\text{cm}^{-2}$  in the concentration range of 2–220  $\mu$ M (and 948.48  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 220-650 µM), that is much higher than those of previous reported enzymatic electrodes. We ascribe this performance to a synergetic effect of following factors: (1) Fused junctions of high-quality graphene fibers connect conductive paths for fast electron transport, effectively eliminating the contact resistance. (2) Unique penetration paths of GFF and intrinsic hydrophily of PB enables fast mass transfer for electrolytes and metabolites. (3) Spontaneous absorption of body liquids improves the utilization of active sites inside the electrode. The textile GFF-PB-GO<sub>x</sub>-CS is applied as a dry sensing patch on human skin for the noninvasive monitoring of glucose with the integration of RI technology, which showed high correlation with the blood glucose level measured by the commercial finger-prick glucometer. We believe the materials and methods pave a way for high-performance noninvasive continuous glucose monitoring (CGM) after extensive clinical measurements are implemented.

#### 4. Experimental section

#### 4.1. Materials

Potassium ferricyanide ( $\geq$  99.95%), ferric chloride anhydrous ( $\geq$  99.9%), potassium chloride (AR), ammonium bicarbonate (AR), sodium chloride (AR), hydrogen peroxide solution (AR, 30 wt% in water), D-(+)-glucose (AR), fructose (99%), ascorbic acid ( $\geq$  99%), dopamine hydrochloride (98%), L-lactic acid ( $\geq$  98%), acetate acid (99.8%), chitosan (degree of deacetylation  $\geq$  95%), and 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid ammonium salt) ( $\geq$  98%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Glucose oxidase from aspergillus niger and Peroxidase from horseradish were purchased from Sigma-Aldrich. Graphene oxide with average lateral size of 20 µm was acquired from GaoxiTech Co., Ltd. All reagents were used as received without any further treatment. Deionized water was generated by PW Ultra-pure Water System (Ulupure, China) and had a resistivity of 18 M $\Omega$  cm.

# 4.2. Wet-spinning of graphene oxide staple fibers

Aqueous GO solution ( $\sim 4 \text{ mg mL}^{-1}$ ) was used as the spinning dope and injected into a rotating coagulation bath with 5 wt% ammonium bicarbonate in water, by a spinneret with diameter of 250 µm. The injection and rotation speeds were set as 50  $\mu L \ min^{-1}$  and 50 r.p.m., respectively.

# 4.2.1. Preparation of non-woven graphene oxide fiber fabrics (GOFFs)

The graphene oxide staple fibers were transferred from above mentioned coagulation bath into a mixture of water and ethanol (volume ratio of 10:1). Then, the fibers were collected by filtration and fused with each other by wet-fusing process. After drying at 100  $^{\circ}$ C for 10 h, a piece of non-woven GOFF was obtained.

# 4.3. Conversion of GOFFs into graphene fiber fabrics (GFFs)

Hydroiodic acid (HI) reduction was firstly performed to obtain rGOFFs by putting the GOFFs into a sealed PTFE reactor filled with a HI aqueous solution ( $\sim 5\%$ )/ethanol (volume ratio of 1:5) mixture and kept at 95 °C for 5 h. After being washed by deionized water and dried at 100 °C overnight, thermal annealing was carried out successively at 1000 and 3000 °C with argon protection for 1 h to convert the rGOFFs to GFFs.

#### 4.4. Electrodeposition of Prussian blue on GFFs

The electrochemical deposition of Prussian blue (PB) was performed in a three-electrode system (GFF working electrode, Ag/AgCl reference electrode, Pt counter electrode) in a solution with 2.5 mM FeCl<sub>3</sub>, 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>], 0.1 M KCl, and 0.1 M HCl. Before deposition, the GFF was pre-treated by plasma for 5 min to make it hydrophilic. The deposition of PB was carried out by applied a potentiostatic voltage of 0.4 V (versus Ag/AgCl) on the GFF for 5 s

#### 4.5. Loading enzyme and protective polymer on electrode

Glucose oxidase (GO<sub>x</sub>) from aspergillus niger was dissolved in PBS (pH = 7) to prepare an aqueous enzyme solution of 20 mg mL<sup>-1</sup>. The solution was then preserved at 4 °C to keep the enzymatic activity. The enzyme solution was dropped onto the surface of GFF-PB and then penetrated into the interspace between graphene fibers. The mass loading of GO<sub>x</sub> on the electrode is about 2.5 mg cm<sup>-2</sup>. After being dried at 4 °C for 12 h, chitosan solution was subsequently dropped onto the GFF-PB-GO<sub>x</sub> electrode to form a protective layer for GO<sub>x</sub>. Note that the chitosan solution was prepared by adding the chitosan powder into a 2% acetic acid solution and stirred at 80 °C for 1 h to obtain a transparent aqueous solution with 5 mg mL<sup>-1</sup> of chitosan.

# 4.6. Characterization and measurements

Morphologies of GOFF, GFF, and GFF-PB were studied using fieldemission SEM (HITACHI SU8010, Japan). Elements distributions were observed by energy dispersive spectrometer (EDS) (HITACHI SU8010, Japan). X-ray photoelectron spectroscopy was carried out by Thermo ESCALAB 250  $\times$  1. X-ray diffraction measurements were performed by Bruker D8 Advance. The wettability of GOFF, GFF and GFF-PB was characterized by a contact angle meter (Biolin Theta, Sweden). Amperometric *I-t* response, cyclic voltammetry, linear sweep voltammetry, and electrochemical impedance spectroscopy based on the threeelectrode system (Fig. S12) were performed by an electrochemical workstation (CHI 660e).

#### 4.7. In vivo glucose measurement experiment

Before tests, the skin surface of subjects was washed with DI water and scrubbed by medical alcohol (75%) for sterilization. The PBS solution ( $\sim$ 30 µL) was used to wet the sensing area and as electrolyte. Invasive glucose measurements were done by a commercial finger-prick glucometer (On•Call Plus) with blood collection needles. Subsequently, noninvasive glucose tests were immediately carried out using the fabricated electrochemical device. To extract interstitial fluid (ISF) in subcutaneous tissues, a bias voltage of -3.0 V was applied between the carbon counter electrode and iontophoretic anode on skin surface for 2 min. The response of glucose in ISF was recorded by amperometric *I*-*t* technology (0.1 V versus Ag/AgCl reference electrode).

#### CRediT authorship contribution statement

Q. Zhang, Z. Li, and Y. Wang conceived the idea. S. Cai and C. Xu designed the materials and devices. S. Cai, C. Xu, D. Jiang, and M. Yuan fabricated devices, performed experiments and analyzed the results. Z. Li, Q. Zhang and Y. Wang helped with manuscript writing. All the authors discussed the results and commented on the manuscript.

#### **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

This work was financially supported by National Key Research and Development Program of China (2017YFC0111300), Zhejiang Province Natural Science Fund for Distinguished Young Scholars (LR19H180001), National Natural Science Foundation of China (52073051), Science and Technology Development Project of Wenzhou Longwan's (2016YG15), Leading Talent Innovation and Entrepreneurship Project of Wenzhou (RX2016005), and Public Projects of Wenzhou (2020005).

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2021.106904.

#### References

- [1] W. Gao, S. Emaminejad, H.Y.Y. Nyein, S. Challa, K. Chen, A. Peck, H.M. Fahad, H. Ota, H. Shiraki, D. Kiriya, D.-H. Lien, G.A. Brooks, R.W. Davis, A. Javey, Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis, Nature 529 (2016) 509–514.
- [2] H.Y.Y. Nyein, W. Gao, Z. Shahpar, S. Emaminejad, S. Challa, K. Chen, H.M. Fahad, L.C. Tai, H. Ota, R.W. Davis, A. Javey, A wearable electrochemical platform for noninvasive, simultaneous monitoring of Ca<sup>2+</sup> and pH, ACS Nano 10 (2016) 7216–7224.
- [3] Y. Chen, S. Lu, S. Zhang, Y. Li, Z. Qu, Y. Chen, B. Lu, X. Wang, X. Feng, Skin-like biosensor system via electrochemical channels for noninvasive blood glucose monitoring, Sci. Adv. 3 (2017), e1701629.
- [4] Y. Lin, M. Bariya, H.Y.Y. Nyein, L. Kivimäki, S. Uusitalo, E. Jansson, W. Ji, Z. Yuan, T. Happonen, C. Liedert, J. Hiltunen, Z. Fan, A. Javey, Porous enzymatic membrane for nanotextured glucose sweat sensors with high stability toward reliable noninvasive health monitoring, Adv. Funct. Mater. 29 (2019), 1902521.
  [5] Y. Lin, J. Chen, M.M. Tavakoli, Y. Gao, Y. Zhu, D. Zhang, M. Kam, Z. He, Z. Fan,
- [5] Y. Lin, J. Chen, M.M. Tavakoli, Y. Gao, Y. Zhu, D. Zhang, M. Kam, Z. He, Z. Fan, Printable fabrication of a fully integrated and self-powered sensor system on plastic substrate, Adv. Mater. 31 (2019), 1804285.
- [6] X. Wei, M. Zhu, J. Li, L. Liu, J. Yu, Z. Li, B. Ding, Wearable biosensor for sensitive detection of uric acid in artificial sweat enabled by a fiber structured sensing interface, Nano Energy 85 (2021), 106031.
- [7] S.K. Vashist, Non-invasive glucose monitoring technology in diabetes management: a review, Anal. Chim. Acta 750 (2012) 16–27.
- [8] J. Kim, A.S. Campbell, J. Wang, Wearable non-invasive epidermal glucose sensors: a review, Talanta 177 (2018) 163–170.
- [9] K.V. Larin, M.S. Eledrisi, M. Motamedi, R.O. Esenaliev, Noninvasive blood glucose monitoring with optical coherence tomography: a pilot study in human subjects, Diabetes Care 25 (2002) 2263–2267.
- [10] M.G. Ghosn, N. Sudheendran, M. Wendt, A. Glasser, V.V. Tuchin, K.V. Larin, Monitoring of glucose permeability in monkey skin in vivo using optical coherence tomography, J. Biophotonics 3 (2010) 25–33.
- [11] H. Shibata, Y.J. Heo, T. Okitsu, Y. Matsunaga, T. Kawanishi, S. Takeuchi, Injectable hydrogel microbeads for fluorescence-based in vivo continuous glucose monitoring, Proc. Natl. Acad. Sci. USA 107 (2010) 17894–17898.

- [12] O.K. Cho, Y.O. Kim, H. Mitsumaki, K. Kuwa, Mitsumaki, Noninvasive measurement of glucose by metabolic heat conformation method, Clin. Chem. 50 (2004) 1894–1898.
- [13] R.K. Shervedani, A.H. Mehrjardi, N. Zamiri, A novel method for glucose determination based on electrochemical impedance spectroscopy using glucose oxidase self-assembled biosensor, Bioelectrochemistry 69 (2006) 201–208.
- [14] X. Yang, A.Y. Zhang, D.A. Wheeler, T.C. Bond, C. Gu, Y. Li, Direct molecule-specific glucose detection by Raman spectroscopy based on photonic crystal fiber, Anal. Bioanal. Chem. 402 (2012) 687–691.
- [15] R.O. Potts, J.A. Tamada, M.J. Tierney, Glucose monitoring by reverse iontophoresis, Diabetes Metab. Res. Rev. 18 (2002) S49–S53.
- [16] S. Iguchi, H. Kudo, T. Saito, M. Ogawa, H. Saito, K. Otsuka, A. Funakubo, K. Mitsubayashi, A flexible and wearable biosensor for tear glucose measurement, Biomed. Micro 9 (2007) 603–609.
- [17] A. Soni, S.K. Jha, A paper strip based non-invasive glucose biosensor for salivary analysis, Biosens. Bioelectron. 67 (2015) 763–768.
- [18] J. Heikenfeld, Non-invasive analyte access and sensing through eccrine sweat: challenges and outlook circa 2016, Electroanalysis 28 (2016) 1242–1249.
- [19] A. Koh, D. Kang, Y. Xue, S. Lee, R.M. Pielak, J. Kim, J.A. Rogers, wearable microfluidic device for the capture, storage, and colorimetric sensing of sweat, Sci. Transl. Med. 8 (2016) 366ra165.
- [20] H. Lee, C. Song, Y.S. Hong, M.S. Kim, H.R. Cho, T. Kang, K. Shin, S.H. Choi, T. Hyeon, D.-H. Kim, Wearable/disposable sweat-based glucose monitoring device with multistage transdermal drug delivery module, Sci. Adv. 3 (2017), e1601314.
- [21] H. Lee, Y.J. Hong, S. Baik, T. Hyeon, D.-H. Kim, Enzyme-based glucose sensor: from invasive to wearable device, Adv. Healthc. Mater. 7 (2018), 1701150.
- [22] L. Lipani, B.G.R. Dupont, F. Dougmene, F. Marken, R.M. Tyrrell, R.H. Guy, A. Ilie, Non-invasive, transdermal, path-selective and specific glucose monitoring via a graphene-based platform, Nat. Nanotechnol. 13 (2018) 504–511.
- [23] C. McCormick, D. Heath, P. Connolly, Towards blood free measurement of glucose and potassium in humans using reverse iontophoresis, Sens. Actuators B Chem. 167 (2012) 593–600.
- [24] A.J. Bandodkar, W. Jia, C. Yard1mc1, X. Wang, J. Ramirez, J. Wang, Tattoo-based noninvasive glucose monitoring: a proof-of-concept study, Anal. Chem. 87 (2015) 394–398.
- [25] M. Aller-Pellitero, J. Fremeau, R. Villa, G. Guirado, B. Lakard, J.-Y. Hihn, F.J. D. Campo, Electrochromic biosensors based on screen-printed Prussian blue electrodes, Sens. Actuators B Chem. 290 (2019) 591–597.
- [26] Z. Chu, J. Peng, W. Jin, Advanced nanomaterial inks for screen-printed chemical sensors, Sens. Actuators B Chem. 243 (2017) 919–926.
- [27] D.W. Hwang, S. Lee, M. Seo, T.D. Chung, Recent advances in electrochemical nonenzymatic glucose sensors-A review, Anal. Chim. Acta 1033 (2018) 1–34.
- [28] J. Kim, J.R. Sempionatto, S. Imani, M.C. Hartel, A. Barfidokht, G. Tang, A. S. Campbell, P.P. Mercier, J. Wang, Simultaneous monitoring of sweat and interstitial fluid using a single wearable biosensor platform, Adv. Sci. 5 (2018), 1800880.
- [29] J. Wang, M. Musameh, Carbon nanotube/teflon composite electrochemical sensors and biosensors, Anal. Chem. 75 (2003) 2075–2079.
- [30] D. Zhai, B. Liu, Y. Shi, L. Pan, Y. Wang, W. Li, R. Zhang, G. Yu, Highly sensitive glucose sensor based on Pt nanoparticle/polyaniline hydrogel heterostructures, ACS Nano 7 (2013) 3540–3546.
- [31] Z. Xu, J. Song, B. Liu, S. Lv, F. Gao, X. Luo, P. Wang, A conducting polymer PEDOT: PSS hydrogel based wearable sensor for accurate uric acid detection in human sweat, Sens. Actuators B Chem. 348 (2021), 130674.
- [32] H. Al-Sagur, K.S. Sundaram, E.N. Kaya, M. Durmus, T.V. Basova, A. Hassan, Amperometric glucose biosensing performance of novel graphene nanoplateletsiron phthalocyanine incorporated conducting hydrogel, Biosens. Bioelectron. 139 (2019), 111323.
- [33] L. Dong, C. Xu, Y. Li, Z. Pan, G. Liang, E. Zhou, F. Kang, Q. Yang, Breathable and wearable energy storage based on highly flexible paper electrodes, Adv. Mater. 28 (2016) 9313–9319.
- [34] M. Zhu, Y. Wang, M. Lou, J. Yu, Z. Li, B. Ding, Bioinspired transparent and antibacterial electronic skin for sensitive tactile sensing, Nano Energy 82 (2021), 105669.
- [35] M. Zhu, M. Lou, J. Yu, Z. Li, B. Ding, Energy autonomous hybrid electronic skin with multi-modal sensing capabilities, Nano Energy 78 (2020), 105208.
- [36] A. Miyamoto, S. Lee, N.F. Cooray, S. Lee, M. Mori, N. Matsuhisa, H. Jin, L. Yoda, T. Yokota, A. Itoh, M. Sekino, H. Kawasaki, T. Ebihara, M. Amagai, T. Someya, Inflammation-free, gas-permeable, lightweight, stretchable on-skin electronics with nanomeshes, Nat. Nanotechnol. 12 (2017) 907–913.
- [37] W. Zhou, S. Yao, H. Wang, Q. Du, Y. Ma, Y. Zhu, Gas-permeable, ultrathin, stretchable epidermal electronics with porous electrodes, ACS Nano 14 (2020) 5798–5805.
- [38] A. Meng, X. Hong, H. Zhang, W. Tian, Z. Li, L. Sheng, Q. Li, Nickel sulfide nanoworm network architecture as a binder-free high-performance non-enzymatic glucose sensor, Microchim. Acta 188 (2021) 1–9.
- [39] H. Xu, H. Chen, C. Gao, Advanced graphene materials for sodium/potassium/ aluminum-ion batteries, ACS Mater. Lett. 3 (2021) 1221–1237.
- [40] H. Chen, H. Xu, S. Wang, T. Huang, J. Xi, S. Cai, F. Guo, Z. Xu, W. Gao, C. Gao, Ultrafast all-climate aluminum-graphene battery with quarter-million cycle life, Sci. Adv. 3 (2017) eaao7233.
- [41] S. Cai, T. Huang, H. Chen, M. Salman, K. Gopalsamy, C. Gao, Wet-spinning of ternary synergistic coaxial fibers for high performance yarn supercapacitors, J. Mater. Chem. A 5 (2017) 22489–22494.

- [42] S. Cai, X. Chu, C. Liu, H. Lai, H. Chen, Y. Jiang, F. Guo, Z. Xu, C. Wang, C. Gao, Water-Salt oligomers enable supersoluble electrolytes for high-performance aqueous batteries, Adv. Mater. 33 (2021), 2007470.
- [43] Z. Li, Z. Xu, Y. Liu, R. Wang, C. Gao, Multifunctional non-woven fabrics of interfused graphene fibres, Nat. Commun. 7 (2016) 13684.
- [44] Z. Liang, J. Zhang, C. Wu, X. Hu, Y. Lu, G. Wang, F. Yu, X. Zhang, Y. Wang, Flexible and self-healing electrochemical hydrogel sensor with high efficiency toward glucose monitoring, Biosens. Bioelectron. 155 (2020), 112105.
- [45] M.A. Zahed, S.C. Barman, P.S. Das, M. Sharifuzzaman, H.S. Yoon, S.H. Yoon, J. Y. Park, Highly flexible and conductive poly (3, 4-ethylene dioxythiophene)-(styrene sulfonate) anchored 3-dimensional porous graphene network-based electrochemical biosensor for glucose and pH detection in human perspiration, Biosens. Bioelectron. 160 (2020), 112220.
- [46] M.A. Yokus, T. Songkakul, V.A. Pozdin, A. Bozkurt, M.A. Daniele, Wearable multiplexed biosensor system toward continuous monitoring of metabolites, Biosens. Bioelectron. 153 (2020), 112038.
- [47] Q. Cao, B. Liang, T. Tu, J. Wei, L. Fang, X. Ye, Three-dimensional paper-based microfluidic electrochemical integrated devices (3D-PMED) for wearable electrochemical glucose detection, RSC Adv. 9 (2019) 5674–5681.
- [48] S. Soylemez, H.Z. Kaya, Y.A. Udum, L. Toppare, A multipurpose conjugated polymer: electrochromic device and biosensor construction for glucose detection, Org. Electron. 65 (2019) 327–333.
- [49] S. Phetsang, J. Jakmunee, P. Mungkornasawakul, R. Laocharoensuk, K. Ounnunkad, Sensitive amperometric biosensors for detection of glucose and cholesterol using a platinum/reduced graphene oxide/poly(3-aminobenzoic acid) film-modified screen-printed carbon electrode, Bioelectrochemistry 127 (2019) 125–135.
- [50] B. Saha, S.K. Jana, S. Majumder, S. Banerjee, An alternative electron transfer process for selective detection of glucose in blood serum, Sens. Actuators B Chem. 283 (2019) 116–123.
- [51] Q. Liao, H. Jiang, X. Zhang, Q. Qiu, Y. Tang, X. Yang, Y. Liu, W. Huang, A single nanowire sensor for intracellular glucose detection, Nanoscale 11 (2019) 10702–10708.
- [52] Z. Xu, C. Gao, Graphene in macroscopic order: liquid crystals and wet-spun fibers, Acc. Chem. Res. 47 (2014) 1267–1276.
- [53] Z. Li, T. Huang, W. Gao, Z. Xu, D. Chang, C. Zhang, C. Gao, Hydrothermally activated graphene fiber fabrics for textile electrodes of supercapacitors, ACS Nano 11 (2017) 11056–11065.
- [54] J. Hu, A. Stein, P. Bühlmann, Rational design of all-solid-state ion-selective electrodes and reference electrodes, TrAC Trends Anal. Chem. 76 (2016) 102–114.
   [55] A.A. Karyakin, Advances of Prussian blue and its analogues in (bio) sensors. Curr.
- [35] A.A. Karyakii, Advances of Prussian blue and its analogues in (bio) sensors, curr. Opin. Electrochem. 5 (2017) 92–98.
   [56] S. Reich, C. Thomsen, Raman spectroscopy of graphite. Philos. Trans. R. Soc, Lond.
- A 362 (2004) 2271–2288.
- [57] A.C. Ferrari, D.M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene, Nat. Nanotechnol. 8 (2013) 235–246.
- [58] G. Moretti, C. Gervais, Raman spectroscopy of the photosensitive pigment Prussian blue, J. Raman Spectrosc. 49 (2018) 1198–1204.
- [59] S.T. Jadhav, S.J. Rajoba, S.A. Patil, S.H. Han, L.D. Jadhav, Temperature-dependent photoluminescence of graphene oxide, J. Electron. Mater. 45 (2016) 379–385.
   [60] X. Chen, X. Wang, D. Fang, A review on C18 XPS-spectra for some kinds of carbon
- [60] X. Chen, X. Wang, D. Fang, A review on C1s XPS-spectra for some kinds of carbon materials, Fuller. Nanotub. Car. Nanostruct. 28 (2020) 1048–1058.
- [61] A. Dias, N. Bundaleski, E. Talarova, F.M. Dias, J. Henriques, Production of Ngraphene by microwave N<sub>2</sub>-Ar plasma, J. Phys. D Appl. Phys. 49 (2016), 055307.
- [62] L. Yu, J. Zhao, S. Tricard, Q. Wang, J. Fang, Efficient detection of ascorbic acid utilizing molybdenum oxide@Prussian blue/graphite felt composite electrodes, Electrochim. Acta 322 (2019), 134712.
- [63] Z. Chu, Y. Zhang, X. Dong, W. Jin, N. Xu, B. Tieke, Template-free growth of regular nano-structured Prussian blue on a platinum surface and its application in biosensors with high sensitivity, J. Mater. Chem. 20 (2010) 7815–7820.
- [64] X. Kang, J. Wang, H. Wu, I.A. Aksay, J. Liu, Y. Lin, Glucose oxidase-graphenechitosan modified electrode for direct electrochemistry and glucose sensing, Biosens. Bioelectron. 25 (2009) 901–905.
- [65] L. Chen, X. Wang, X. Zhang, H. Zhang, 3D porous and redox-active prussian bluein-graphene aerogels for highly efficient electrochemical detection of H<sub>2</sub>O<sub>2</sub>, J. Mater. Chem. 22 (2012) 22090–22096.
- [66] S. Park, T.D. Chung, H.C. Kim, Nonenzymatic glucose detection using mesoporous platinum, Anal. Chem. 75 (2003) 3046–3049.
- [67] J. Yang, Y.G. Nam, S.K. Lee, C.S. Kim, Y.M. Koo, W.J. Chang, S. Gunasekaran, Paper-fluidic electrochemical biosensing platform with enzyme paper and enzymeless electrodes, Sens. Actuators B Chem. 203 (2014) 44–45.
- [68] J. Kim, J.R. Sempionatto, S. Imani, M.C. Hartel, A. Barfidokht, G. Tang, A. S. Campbell, P.P. Mercier, J. Wang, Simultaneous monitoring of sweat and interstitial fluid using a single wearable biosensor platform, Adv. Sci. 5 (2018), 1800880.



Shengying Cai received his B.S. in materials science and engineering from Zhejiang Sci-Tech University, China in 2014 and received his Ph.D. degree in polymer chemistry and physics from the Department of Polymer Science and Engineering, Zhejiang University, China in 2020. He is now a post doctor at Wenzhou Institute, University of Chinese Academy of Sciences.





**Danfeng Jiang** received his B.S. in chemical engineering from the Department of Chemistry and Chemical Engineering, Nantong University, China in 2014 and received his Ph.D. degree in chemical engineering from the Department of Chemical Engineering, Nanjing Tech University, China in 2019. He is now a research assistant professor at Wenzhou Institute, University of Chinese Academy of Sciences.



**Meiling Yuan** received her B.S. in biomedical engineering from Jinggangshan University, China in 2016. Now, she is a Master degree candidate in Wenzhou Medical University.



Qingwen Zhang is an associate professor at Wenzhou Institute, University of Chinese Academy of Sciences. She received her Ph.D. degree in physical chemistry from the Department of Chemistry and Chemical Engineering, Beijing Institute of Technology (BIT), China in 2014. She joined in the Wolfgang Knoll group of Austrian Institute of Technology (AIT) as a visiting scholar from December 2010 to November 2011. Since joining the current working unit from 2015, she has carried out the research on the preparation of biological and composite nanomaterials for the development of wearable biosensors, electrochemical sensors and SPR micro imaging sensors.

#### Nano Energy 93 (2022) 106904





**Prof. Zhaoling Li** obtained his Ph.D. degree from Donghua University, China majoring in Textile Engineering in 2016. He was once serving as a Visiting Scholar in Georgia Institute of Technology, USA for one year and a half. He is now a Professor in the College of Textiles in Donghua University. His research focuses on triboelectric nanogenerator, pressure sensor, wear-able biosensor, and electronic skin for energy, sensing, environment, and electronic applications in the form of functional fibers and smart textiles. He has already published more than 60 SCI papers, coauthored 2 book chapters and has authorized 21 invention patents.



**Prof. Yi Wang** received his Ph.D. degree from Max-Planck Institute, Germany in 2010. After that he worked as a research fellow at Austrian Institute of Technology and Nanyang Technological University from 2011 to 2015. He is now a Professor at Wenzhou Institute, University of Chinese Academy of Sciences, and Wenzhou Medical University. He has published over 60 peer-reviewed journal papers on nanomaterials-based biosensors. His research interests include the development of plasmonic nanostructure, nanocomposites, novel polymers and peptide-functionalized materials for optical and electrical biosensors.