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All Inkjet-Printed Amperometric Multiplexed Biosensors Based on Nanostructured Conductive Hydrogel Electrodes

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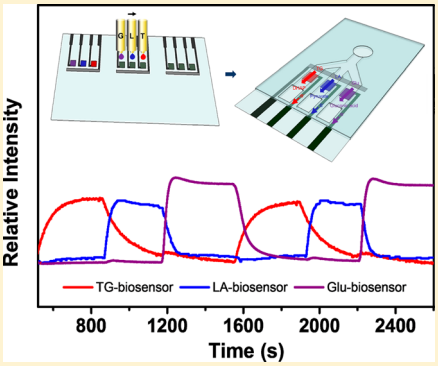
Supporting Information

ABSTRACT: Multiplexing, one of the main trends in biosensors, aims to detect several analytes simultaneously by integrating miniature sensors on a chip. However, precisely depositing electrode materials and selective enzymes on distinct microelectrode arrays remains an obstacle to massively produced multiplexed sensors. Here, we report on a "drop-on-demand" inkjet printing process to fabricate multiplexed biosensors based on nanostructured conductive hydrogels in which the electrode material and several kinds of enzymes were printed on the electrode arrays one by one by employing a multinozzle inkjet system. The whole inkjet printing process can be finished within three rounds of printing and only one round of alignment. For a page of sensor arrays containing 96 working electrodes, the printing process took merely ∼5 min. The multiplexed assays can detect glucose, lactate, and triglycerides in real time with good selectivity and high sensitivity, and the results in phosphate buffer solutions and calibration serum samples are comparable. The inkjet printing process exhibited advantages of high efficiency and accuracy, which opens substantial possibilities for massive fabrication of integrated multiplexed biosensors for human health monitoring.



KEYWORDS: *inkjet printing, multiplex, biosensor, polyaniline, hydrogel*

Human health is a global concern that requires improved methods to assess health status, monitor the initiation and progression of disease, and evaluate treatment outcomes.[1,2] Clinical medical studies found that the occurrence of some diseases is highly related to the abnormality of more than one metabolite in the human body;[3,4] for example, cardiovascular disease may be due to the presence of one or more risk factors, such as diabetes or hyperlipidemia.[5] Diabetes often results from abnormally high blood sugar levels and is coupled with many complications.[6] High levels of triglycerides can cause atherosclerosis, vascular blockage, and thrombosis and can increase the risk of cardiovascular disease.[7] The blood lactate level reflects the status of metabolism, and an increase in lactate concentration can predict multiple organ failure and death in patients with septic shock.[8] Recently, lactate was proposed to be the most important energy carrier for cancer cells.[9] Moreover, patients with diabetes are prone to diabetic lactic acidosis.[10] Hence, the presence of multiple metabolic disorders increases the risk to human health because metabolites in the human body are synergistic and thus require multiplex assays.

Multiplexed detection of several metabolite levels within a single biosensor chip would be helpful for either accurately diagnosing/treating a specific disease or reducing the quantity of blood needed for comprehensive physical examination in the clinic.[11−13] However, the scalable fabrication of multiplexed biosensors remains a challenge because it involves the precise patterning and alignment of electroactive/immobilizing materials and different kinds of enzymes on selective electrode arrays. Traditional photolithography technology is not particularly compatible with the patterning of these soft materials.[14,15] Screen printing can be used for massive fabrication, but it needs complex alignment for each layer and may waste enzyme slurry, which is the most expensive component in biosensors.[16] Electronic printing technology is an alternative choice for the low-cost and massive production of electronic devices,[17,18] but to the best of our knowledge, it has not yet been used to produce amperometric multiplexed biosensors.[19−22] In this report, we describe a "drop-on-demand" inkjet print strategy to fabricate multiplex biosensors. A drop-on-demand process uses software that directs the printer to generate individual drops, which are only jetted onto the spot where it is needed.[23] Hence, we can selectively print different enzymes onto the desired area. By employing a digital multinozzle three-axis inkjet print system, a conductive polymer hydrogel and several kinds of enzymes were printed on the electrode arrays one by one. The total inkjet printing process can be finished within three rounds of printing and needs only one round of alignment. For a page of sensor arrays containing 96 working electrodes, printing took merely ∼5

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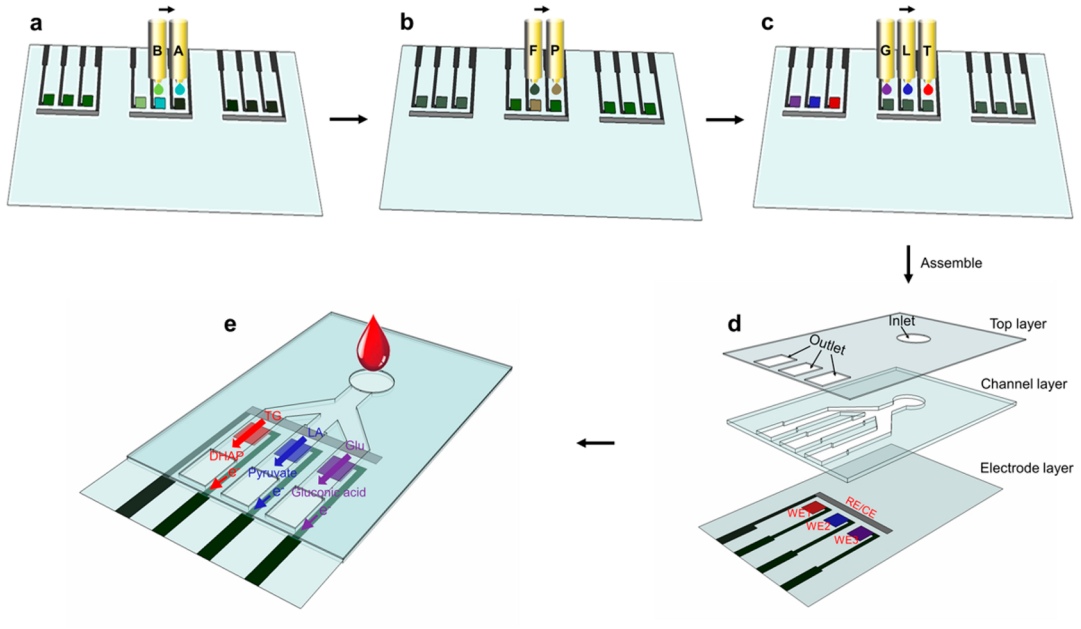

Figure 1. Schematic illustration of the design and fabrication of the inkjet-printed multiplexed biosensor based on conductive hydrogels. (a) Precursor solutions A and B were printed on the predefined areas to form a PAni hydrogel on the working electrode (WE). (b) Chloroplatinic acid (P) and formic acid (F) solutions were printed to generate platinum nanoparticles (PtNPs) on the PAni hydrogel film. (c) Enzyme solutions G (glucose oxidase solution, GOx), L (lactic oxidase solution, LOx), and T (mixed solution of lipase/glycerol kinase/L-α-glycerophosphate oxidase, LP/GK/GPO) were then sequentially printed onto their corresponding electrodes one by one. (d) The multiplexed biosensor was assembled by integrating the top layer, channel layer, and electrode layer. (e) Schematic of the multiplexed detection of metabolites in human blood with the multiplex assay.

min. Our printed multiplex assay achieved biosensing with good selectivity and high sensitivity; for example, it detected triglycerides with a sensitivity of 7.49 μA mM^{-1} cm^{-2} between 0.1 and 6 mM, lactate with a sensitivity of 3.94 μA mM^{-1} cm^{-2} between 0.08 mM and 5 mM, and glucose with a sensitivity of 5.03 μA mM^{-1} cm^{-2} between 1 and 25 mM. Furthermore, the multiplex sensors worked reproducibly in both standard phosphate buffer solutions and human serum samples.

The multiplexed biosensor consisted of an electrode layer, a microfluidic channel layer, and a top cover as shown as Figure 1. The biosensors were printed on the electrode layer, which is a piece of polyethylene terephthalate (PET) film with 6 × 8 prescreen-printed electrode units. Each unit contains three screen-printed carbon paste working electrodes and a Ag/AgCl electrode (Figure S1). The printed Ag/AgCl electrode acts as a shared reference electrode and counter electrode for both biosensors.[3,24] The conductive polymer polyaniline (PAni) hydrogel as interfacial material was deposited in the first round of inkjet printing with two nozzles. Aqueous solution A (phytic acid and aniline) and solution B (ammonium persulfate as an initiator) were over-printed on the working electrodes sequentially. Even though the smallest droplet from the inkjet printer is 0.1 μL, we select a 3 μL volume so that only one droplet needs to be printed on one electrode spot, as it can completely wet and cover the electrode area. It is worth noting that the carbon paste electrode has been treated to be more hydrophilic than the PET substrate (contact angle (CA) of carbon paste is ∼45.5° and that of PET is ∼77.6°, as shown in Figure S2). The predefinition of the hydrophilic electrode area greatly lowered the requirement of printing precision because the droplets will automatically wet over the electrode area once they are deposited into the area. The mixed solution quickly formed a PAni hydrogel thin film on the electrode.[25] Next, formic acid and chloroplatinic acid solutions were applied to the electrode for the homogeneous high-density loading of the PtNPs (Figure 1b).

The enzyme solutions were then printed via the "drop-on-demand" strategy onto the designated working electrode areas after purification of the PAni hydrogel and an alignment operation over the marks on the substrate (Figure 1c). Solution T is a mixed solution of lipase (LP), glycerol kinase (GK), and L-α-glycerophosphate oxidase (GPO) for the detection of triglycerides. Solution L is lactic oxidase (LOx), and solution G is glucose oxidase (GOx). Because of the highly porous and hydrophilic nature (CA ∼26.7°, Figure S2c) of the PAni hydrogel, printed enzyme droplets can be absorbed into the PAni matrix. Next, for the enzymes to be cross-linked with the PAni hydrogel film, glutaraldehyde was applied onto the substrate. The deposition of various enzymes onto the corresponding electrodes can be performed precisely and efficiently without wasting any of the enzymes, which is in sharp contrast to screen printing. Note that enzymes are the costliest component of biosensors: some of them are even more expensive than gold. Furthermore, all of the printing procedures took only ∼5 min to fabricate 32 devices (96 electrodes), revealing the strong massive production potential of digitally controlled inkjet printing.

Another typical challenge for fabricating multiplexed sensors involves the interfacial material between biological systems and electrodes,[26−28] which usually acts both as an immobilization matrix for enzymes and as an electrical connector. To this end, many nanomaterials have been investigated.[29−31] However, most of them are researched separately, i.e., used to detect only one substrate in one procedure; therefore, some of these materials could be very sensitive to one substrate, but it is unknown whether they are as sensitive to other substrates and whether there is interference between different substrates. Therefore, developing biosensors that synergistically detect several substrates would be helpful for the future development of

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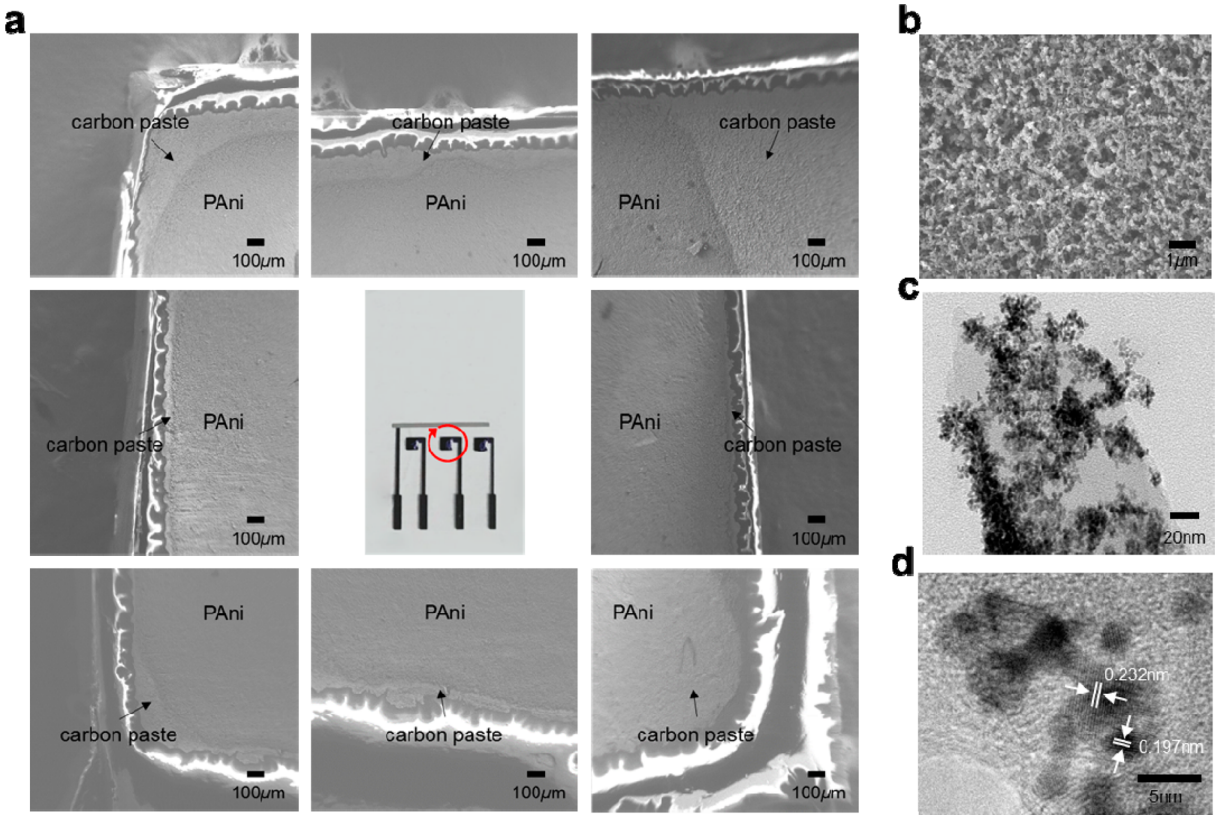

Figure 2. Structures of the printed PAni hydrogel/PtNP heterostructures. (a) Photograph of the device with the printed PAni hydrogel (center) surrounded by SEM images revealing the boundary of the formed PAni hydrogel film on the predefined hydrophilic zone of a carbon paste electrode. (b) SEM image of the PAni hydrogel formed on the working electrode. (c) TEM image of the PtNP-modified PAni hydrogel indicating the high-density loading of PtNPs. (d) HR-TEM image of the PtNPs on the PAni hydrogel.

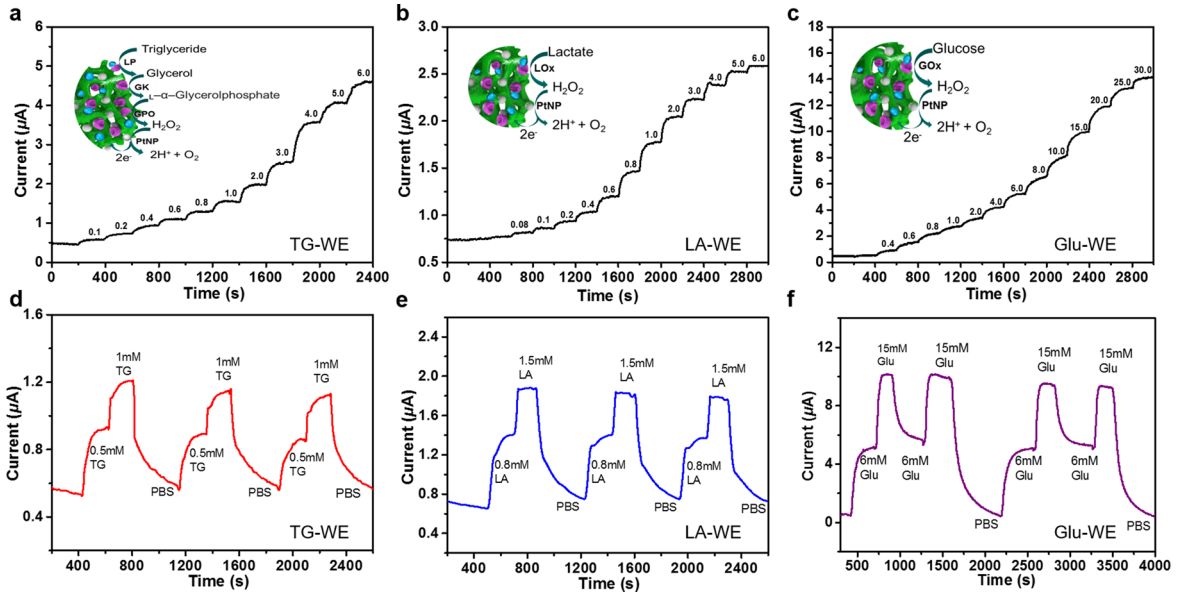

Figure 3. Instant current−time response curves and repeatability of printed biosensors when metabolite solutions with different concentrations were pumped into the channel in an alternating manner (flow velocity: 200 μL/min). (a, d) TG-WE detects triglyceride. (b, e) LA-WE detects lactate. (c, f) Glu-WE detects glucose. The insets in (a−c) show the schematic sensing mechanisms of the corresponding metabolites by the PAni hydrogel/PtNP enzymatic biosensors.

multiplexed sensors.[32,33] In this study, we used a polyaniline (PAni, a kind of conductive polymer) hydrogel that can be loaded onto virtually any surface as the interfacial electrode material.[34] The PAni hydrogel developed offers several advantages, including high conductivity, good biocompatibility, and excellent biosensing performance.[35−37]

The structures of the printed PAni hydrogel and enzymes were investigated. The PAni hydrogel obtained from 3 μL of precursor

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solution formed a film exactly covering the predefined hydrophilic working electrode area, as shown as Figure 2a and Figure S3. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Figure 2b and Figure S4a−c reveal the three-dimensional (3D) hierarchically porous micro/nano-structure of the PAni hydrogel, which consists of interconnected nanofibers with diameters of ∼100 nm. Panels c and d in Figure 2 confirm that Pt nanoparticles (NPs) were uniformly dispersed on the surface of PAni nanofibers (Figure S4d−f). As shown as Figure S4g−i, enzymes were well loaded onto the PAni hydrogel. The compound glutaraldehyde linked the PAni fibers and enzymes by forming covalent C═N bonds, as confirmed by Fourier transform infrared (FT-IR) spectroscopy (Figure S5).[35,37]

The multiplexed biosensor was assembled by integrating the modified electrode layer together with a microfluidic channel layer and a predefined inlet/outlet top layer (Figure 1d). The integrated biosensor is flexible and bendable (Figure S1c). Test liquid is flowed through microfluidic channels to different working electrodes (Figure 1e). The three working electrodes, marked as TG-WE, LA-WE, and Glu-WE, are for the detection of triglycerides, lactate, and glucose, respectively. The amperometric sensing was based on the detection of hydrogen peroxide generated in enzymatic reactions, namely, the reactions between oxidoreductase and the pertinent substrate, which produce hydrogen peroxide in the presence of oxygen; then, the produced hydrogen peroxide was catalytically oxidized by the PtNPs to generate electrons.[38,39] The hydrophilic porous microstructure of the PAni hydrogel was favorable for the transportation of metabolite molecules, and its interconnected fiber structure can facilitate the transport of electrons generated in the enzymatic reactions.

First, metabolites were tested with the corresponding biosensor in the multiplex assay in phosphate buffer saline (PBS), and it was found that the current signals between each working electrode and the Ag/AgCl reference/counter electrode are proportional to the concentration of the corresponding metabolites. Normal concentrations of triglycerides are in the range of 0.4−1.8 mM for a healthy human, and abnormally high triglyceride levels are a risk factor for cardiovascular disease. The detection of triglycerides was realized based on the synergistic interaction of multiple enzymes, as schematically illustrated in the mechanism in the inset of Figure 3a. The triglyceride sensor shows a sensitivity of 7.49 μA mM^{-1} cm^{-2} between 0.1 and 6 mM (Figure S6a). Blood lactate is the metabolic intermediate of sugar in the human body, and the normal concentration of lactate should be 0.5−1.7 mM. An increase in lactate concentration can cause lactic acidosis. The lactate detection is based on lactate oxidase (LOx), which converts lactate to pyruvate and hydrogen peroxide in the presence of oxygen (inset of Figure 3b). Figure 3b shows the amperometric detection of lactate with the working electrode with PAni/PtNPs/LOx. The lactate biosensor has a sensitivity of 3.94 μA mM^{-1} cm^{-2} between 0.08 and 5 mM (Figure S6b). The fasting blood glucose (FBG) concentration of a normal person is usually 3.61−6.11 mM. A person can be diagnosed with diabetes if the random blood glucose (RBG) concentration is greater than 11.1 mM, and a glucose level below 2.8 mM indicates a patient with hypoglycemia. The response currents with the PAni/PtNPs/GOx-modified working electrode are recorded in Figure 3c. The glucose sensor shows good detection performance at concentrations between 1 and 25 mM with a sensitivity of 5.03 μA mM^{-1} cm^{-2} (Figure S6c). The linear range of these sensors can meet the sensing requirement of metabolic levels in the human body. The limit of detection (LOD) of the printed biosensors for the detection of triglycerides, lactate, and glucose are calculated to be 0.07, 0.06, and 0.2 mM with a signal-to-noise ratio (SNR) of ∼3, respectively.

The capability to sense both increases and decreases in substrate concentration, namely, reversibility, is another important parameter of biosensors and is a requirement for a continuously working sensor.[40,41] The sensor assay exhibited a quick response and good repeatability when alternating concentrations of metabolite solutions were pumped into the device, as shown in Figure 3d−f. It is noteworthy that the current saturation times read from Figure 3e and f are not a real value of the response time of the integrated biosensors. Because a peristaltic pump was used in the experiment, it takes time for the solutions to mix and reach the working zone of biosensors. The speed of pumping and the mixed gradient of the solutions in microchannels affect the time for the device to respond. Under these conditions, the real response time of the device is hard to evaluate.

Second, the simultaneous multiple detection of triglycerides, lactate, and glucose was carried out by pumping solutions containing different metabolites into the multiplex assay sequentially. As shown as Figure 4, 0.8 mM triglyceride solutions were pumped into the channel at a flow velocity of 200 μL/min and arrived at different working electrodes simultaneously. Only the TG-WE biosensor showed an obvious current response, and LA-WE and Glu-WE exhibited a slight decrease. When 0.6 mM lactate solutions were pumped in, LA-WE responded, whereas the other two sensors had no response. After that, the fluid was changed to 6 mM glucose solution: Glu-WE exhibited a rapid response, and the other two electrodes showed no response. When the pumping of different metabolite solutions was repeated, the multiplex detection of triglycerides, lactate, and glucose shows good repeatability and excellent reversibility with almost no interference. In addition, the amperometric response of the multiplex biosensors to some usual interfering components at their normal physiological levels was then measured by subsequently pumping different solutions into the device as shown as Figure S7. The levels of interference were mild, and there was almost no impact on the detection of the target metabolites. Additionally, we investigated the stability of the inkjet-printed biosensors as shown in Figure S8. The biosensors still maintain good detection performance after 3 weeks.

Finally, calibration serum samples were tested on the multiplex biosensors, and the results were compared with those obtained with the samples in PBS. Direct sensing using serum samples is one of the largest challenges for biosensors because the physiological and pathological environments in blood are complex. Metabolite solutions in calibration serum and PBS were alternately pumped into the multiplex essay, and the amperometric responses are recorded in Figure 5 and Figure S9. It was found that the values measured in serum and PBS are comparable. The results of the continuous testing of three serum samples were almost the same, revealing that detection with the multiplex biosensors was repeatable.

In conclusion, a "drop-on-demand" inkjet printing strategy was developed to fabricate multiplexed biosensors based on nanostructured conductive hydrogels in which all of the materials and enzymes were selectively printed on the electrode arrays by using a multinozzle three-axis inkjet printing system. This digitally controlled printing system exhibits a strong fabrication

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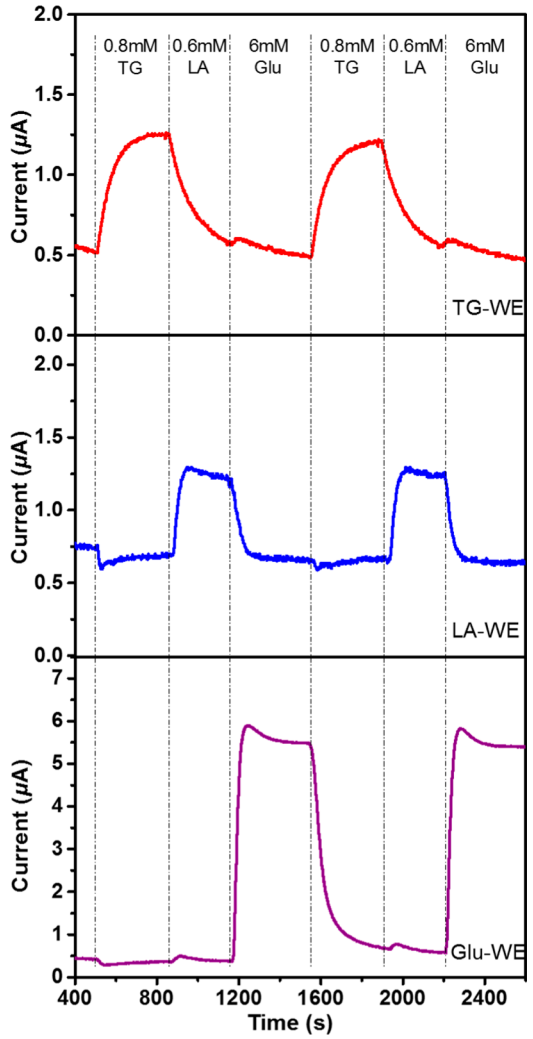

Figure 4. Detecting metabolites with the multiplexed essay. The curves correspond to the instant current collected on different electrodes when metabolite solutions were successively mixed and pumped into the essay with a peristaltic pump (flow velocity: 200 μL/min).

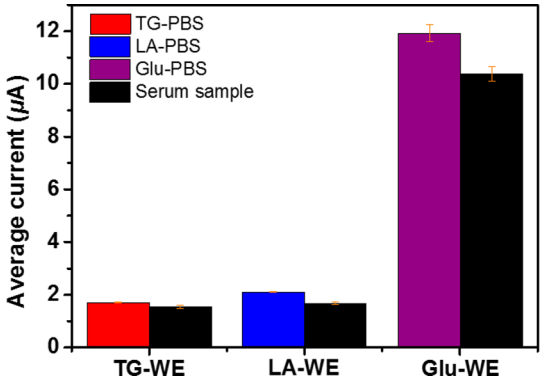

Figure 5. Comparison of the current detected in metabolite solutions in PBS and calibration serum. The concentration of solution with PBS buffer is prepared according to calibration serum sample (triglyceride: 1.1 mM, lactate: 1.45 mM, glucose: 14.9 mM).

capability compared to that of traditional fabrication methods such as screen printing, especially for producing multiplexed sensors, which involves several deposition steps of the electrode material and enzymes on designated electrodes. The method shows substantial advantages, namely, its low cost, high efficiency, and accuracy. The printed multiplexed assays can detect glucose, lactate, and triglycerides in real time with good selectivity and high sensitivity and worked reproducibly in both standard PBS and human serum samples. We envision that this digitally controlled inkjet printing technology will open up substantial possibilities for the massive fabrication of integrated multiplexed biosensors for human health monitoring.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b00003.

Materials and additional experimental procedures and supporting data (PDF)

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Notes

The authors declare no competing financial interest.

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