Ultra-highly conductive hollow channels guided by a bamboo bio-template for electric and electrochemical devices

Omar G. Pandoli,* Reginaldo J. G. Neto, Natália R. Oliveira, Ana C. Fingolo, Cátia C. Corrêa, Khosrow Ghavami, Mathias Strauss* and Murilo Santhiago*

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Ultra-highly conductive hollow channels guided by a bamboo bio-template for electric and electrochemical devices†

Omar G. Pandoli, a Reginaldo J. G. Neto, b Natália R. Oliveira, b Ana C. Fingolo, b Cátia C. Corrêa, b Khosrow Ghavami, a Mathias Strauss a,b, and Murilo Santhiago a, b, c

Fabrication of well-aligned arrays of microfluidic channels is very challenging using conventional microfabrication processes. On the other hand, nature is unique in creating complex hierarchical architectures. For instance, wood-derived materials present well-aligned microchannels that offer the possibility to add new functionalities to biological templates, such as high conductivity necessary for electric and electrochemical devices. However, one of the challenges is to address electrical properties without clogging cellulose-based channels. In this work, a new regioselective coating method is reported to prepare three-dimensional functional conductive structures using bamboo as a bio-template. Silver ink was flowed inside bamboo vascular bundles and excess of the material was removed to prepare ultra-highly conductive coatings that did not block its channels. The conductivity of the hollow channels was 9.3 (±4.0) × 10^5 S m^{-1}, which is the highest value reported for cellulose-based ordered materials. Such remarkable feature enabled the fabrication of unprecedented electrical and electrochemical devices. For example, three-dimensional circuits, microfluidic heaters and fully integrated nanostructured carbon-based electrochemical cells were fabricated using bamboo with fast and low-cost prototyping processes. Moreover, the present work opens a plethora of possibilities to incorporate conductors, semi-conductors and insulating materials for the next generation of electric and electrochemical ‘bambootronic’ bio-devices.

Introduction

Fabrication of three-dimensional (3D) electronic and electrochemical devices has attracted enormous attention due to their potential applications in energy storage, biomedical devices and electronic systems. Recently, 3D fabrication techniques such as controlled folding, 3D printing and templated growth have been used to create interesting structures for these applications. Despite great advances in this area, highly oriented structures at the nano- and microscale are still difficult to fabricate using conventional routes. In order to explore novel architectures, biological structures have been used as bio-templates for the fabrication of greener functional devices. In this regard, nature is very unique in creating complex 3D structures and is of paramount importance in understanding the complexity of living systems, and their hierarchical and anisotropic structures. It is already evident that the incorporation of metal–organic frameworks (MOFs), conductive organic polymers and single-walled carbon nanotubes (SWCNTs) into plant material serves to increase or add new functionalities to vegetal biomass, to promote a new field of plant science and bio-nanotechnology devices.

Regarding the fabrication process, two main classes of cellulose-based materials have been used to obtain functional devices with high electrical conductivity: (i) processed cellulose-based fibers (such as paper) and (ii) raw cellulosic materials. Paper, for instance, has been used as a substrate for a myriad of flexible electronic and electrochemical devices. Conductive materials can be incorporated in the porous structure of paper by exploring the capillary flow of reagents and nanomaterials to fabricate 3D devices by using folding steps. The current limitations of paper are the poor lateral resolution of conductive channels and slow modification process. Another approach consists of using raw cellulose-based materials where most of the biological structure formed by nature is preserved. Wood-
derived materials, for instance, have been shown to have huge potential for many applications in the field of flexible electronics and energy applications, among others.\textsuperscript{28} The presence of highly oriented channels in such materials gives rise to different anisotropic mechanical,\textsuperscript{31} electrical\textsuperscript{32} and thermal properties.\textsuperscript{33} For instance, cellulose membranes with highly aligned cellulose nanofibers can work as ionic conductors and generate electricity when the electrodes located at the extreme ends are exposed to different temperatures.\textsuperscript{34} In addition, internal channels can be impregnated with carbon-based nanotubes to allow transport of ions, oxygen (O\textsubscript{2}) and electrons for energy-based devices.\textsuperscript{35} Carbon nanotubes coated on flexible wood membrane were also demonstrated as a highly efficient solar steam generation device.\textsuperscript{36} Conductive graphene nanosheets can be obtained from calcined waste paper via a facile and inexpensive method.\textsuperscript{37} This carbonization process has been used to produce conductive carbon materials for sensors,\textsuperscript{38} electrodes\textsuperscript{39,40} and supercapacitors.\textsuperscript{41,42} However, the lack of an insulating structure is a major limitation in the integration of more electrodes on the pyrolyzed material. A CO\textsubscript{2} laser can locally pyrolyze the wood surface to fabricate arrays of conductive tracks.\textsuperscript{43} However, the mechanical properties of the pyrolyzed material are poor for robust electronics and electrochemical applications.\textsuperscript{37} Recently, an elegant way to fabricate complex conductive structures using the internal channels of wood was reported.\textsuperscript{44} A conductive wood-based material was prepared by impregnation of a low temperature fused metal alloy (Sn–Bi) into wood vessels, with an excellent conductivity of 5.4 \times 10^{4} S m\textsuperscript{-1} when measured parallel (\sigma\textsubscript{||}) to the channel alignment direction. However, to preserve the naturally occurring hollow channels and expand the applications of such materials, two major limitations need to be addressed. First, fabrication of metallic wood composites requires a heating temperature of 150 °C to reach the alloy melting point and some cellulose-based materials start their thermal degradation process at such temperature.\textsuperscript{45} Second, the metallic alloy clogs the highly oriented channels and strongly limits several applications and fabrication of more complex 3D devices. For example, clogged channels do not allow the fabrication of microfluidic devices or incorporation of conductive pastes. Thus, a new route that achieves high conductivity with lower energy cost and does not promote any obstruction of the vascular microchannels is crucial to the development of new, greener, and sustainable functional devices from vegetal biomass.

Herein, we developed for the first time a room temperature fast prototyping method to fabricate ultra-highly conductive arrays of microchannels using a bamboo anisotropic lignocellulosic structure as a new bio-template. Considering its lightweight and strong mechanical properties,\textsuperscript{46,47} bamboo is the best raw biomass candidate to be explored as a lignocellulosic natural resource for scalable production of eco-friendly, sustainable, low-cost, and portable electronic and electrochemical biodevices. Our method consists of flowing silver ink through the microchannel arrays of bamboo (Dendrocalamus giganteus) and removing the excess ink by flowing nitrogen (N\textsubscript{2}). We achieved a conductivity of 9.3 (±4.0) \times 10^{5} S m\textsuperscript{-1} (\sigma\textsubscript{||}), which is the highest value reported so far for tracks along the vascular network of lignocellulose-derived materials. Moreover, hollow conductive channels enabled the fabrication of unprecedented electronic and electrochemical bamboo-based devices that we call “bambootronic” technology. As a proof of concept, we present 3D electrical circuits, a multi-channel microfluidic heater, and fully integrated carbon-based electrochemical cells.

Experimental

Materials and chemicals

All chemicals were of analytical grade. Potassium chloride, sodium phosphate dibasic, sodium phosphate monobasic, potassium ferricyanide, potassium ferrocyanide trihydrate, iron(III) chloride hexahydrate, and potassium hexacyanoferrate(II) trihydrate were acquired from Sigma-Aldrich, SP, Brazil. Hydrogen peroxide was acquired from Merck, Brazil. Carbon Black (CB) type XC-72R was acquired from Cabot Corporation. Silver ink from SPI Supplies, PA, USA was used to construct the conductive bamboo samples.

All the solutions were prepared by using purified deionized water (18.2 MΩ cm\textsuperscript{-1}) from an Elga Veolia model Purelab Option-Q, UK. An analytical balance from Shimadzu (AUW220D, SP, Brazil), accurate to 5 decimal places, was used to weigh all the reagents and the pH values of all the solutions were determined using a pH meter from Marconi (MA522, SP, Brazil). All the characterization experiments were performed on freshly prepared samples.

Preparation of unmodified and modified carbon black paste

Unmodified carbon black paste was prepared by gently mixing carbon black with mineral oil (Nujol) for 20 min with a mixing ratio of 60 : 40 [(CB/MO) (w/w)]. In order to prepare the modified carbon black paste (carbon black + Prussian blue, denoted as CB-PB), 50 mL of FeCl\textsubscript{3} (0.16 mg mL\textsuperscript{-1} in H\textsubscript{2}O) was added dropwise into 20 mL of deionized water containing 250 mg of carbon black and 8.5 mg of the salt K\textsubscript{3}Fe(CN)\textsubscript{6}. The resulting volume was separated into two tubes of 20 mL each and centrifuged (Sorvall, RC6+, Thermo Scientific) at 15 000 rpm for 30 minutes. The supernatant was removed and 20 mL of deionized water further added to each tube. This process (centrifuge/wash) was repeated four times. Before use, the resulting material (CB-PB) was kept in a vacuum oven at 45 °C for 18 hours. CB-PB was prepared by replacing the bare carbon black with CB-PB via the preparation described above.

Preparation of the conductive bamboo samples

First, the internode section of a bamboo (Dendrocalamus giganteus) culm of 4 years aged from a botanical garden of PUC-RIO was cut into a cylindrical shape with 20 mm length and 6 mm diameter using a methodology already reported in our previous work.\textsuperscript{48} For the removal of the starch present on the bamboo microchannels, the samples were immersed in deionized water at 65 °C and stirred for 30 min. Then, the deionized water was forced to flow through the bamboo microchannel with the help of a syringe pump. The water was then replaced
and the heating and rinsing steps were repeated four times. Finally, the bamboo samples were dried in an oven at 70 °C for 2 hours. For the construction of the conductive bamboo samples, 1.5 mL of the silver ink was forced to flow through the bamboo microchannels with the help of a vacuum pump for 1 min. Plastic tubing was connected at one side of the bamboo to create a silver ink reservoir, while a vacuum pump connector was plugged at the other end of the sample. Next, the ink was dried by flowing N₂ at 2 bar for 30 min through the bamboo microchannels. Later, a stainless-steel razor blade was used to cut thin slices of 1 mm thickness at both sides of the bamboo to remove any residual ink on the surfaces and also to keep the entrance of the microchannels open.

Construction of the 3D bamboo-based working electrode (BWE)

First, to create a hydrophobic layer on the bamboo-based electrodes, a thin layer of epoxy resin (Araldite Hobby Brascola, SC, Brazil) was added at the top face of the bamboo specimen. Just after the addition of the resin, N₂ at 1 bar was flowed through the bamboo sample in order to keep its microchannels opened over the resin reticulation time. Then, epoxy resin was also spread over the side walls of the bamboo sample. On the bamboo’s bottom face, without the epoxy resin coating, the microchannels were short-circuited by the addition of a thin layer of silver ink. Then, the top face coated with epoxy was gently pressed against a Petri dish containing the carbon black paste for 10 min. After this period, filter paper was used to remove any residual ink on the surfaces and also to keep the electric double layer capacitance. Impedance experiments were performed at the open circuit potential (0.16 V vs. Ag/AgCl for bamboo) using the Fe(CN)₆⁴⁻/⁻ redox probe; the perturbation voltage was 10 mV in the frequency range from 0.1 to 10⁵ Hz.

Construction of the 3D fully integrated bamboo-based electrochemical cell (BEC)

A thin layer of epoxy resin was spread on the top face of bamboo as described above. At the bottom face of the bamboo not coated with epoxy three isolated regions corresponding to the reference electrode (RE), working electrode (WE) and counter electrode (CE) were coated with the silver ink. The largest region was assigned to the CE (∼1/2 of the total surface), while smaller regions were assigned to the WE and RE, ∼1/4 respectively (Fig. S1†). Then, microchannels corresponding to the RE area on the epoxy-coated top face were short-circuited with the silver ink. The same RE area was covered with adhesive tape (Scotch® Tape 3M) and the bamboo sample was free from the carbon paste as described for the BWE. For the production of the Ag/AgCl RE, the adhesive tape was removed and 10 µL of a commercially available solution of sodium hypochlorite 2.5 g L⁻¹ (Bufalo, SP, Brazil) was placed on the RE area for 10 min, followed by two rinse steps with deionized water. Finally, three folded aluminum foil strips were connected to the corresponding WE, RE and CE regions on the top face of the BEC. For the electrocatalytic experiments, the CB paste was replaced by the CB-PB paste. (A schematic representation of the methodology is shown in Fig. S1 and S2†)

Electrochemical measurements

All the electrochemical measurements were conducted using the bamboo-based electrodes (BEC and BWE). The cyclic voltammetry experiments were performed using a PGSTAT-204 model from AUTOLAB (Eco Chemie, Netherlands) interfaced by a computer and controlled by NOVA 2.0 software. Typically, 10 mL of the Fe²⁺/Fe³⁺ solution was added to the electrochemical cells. Cyclic voltammetry was used to obtain the capacitance of the bamboo-based fully integrated cell. The current was collected at 0.0 V vs. Ag/AgCl at different scan rates (0.04–0.2 V s⁻¹) in 0.5 M KCl solution. The width of the voltammogram (I_anodic + I_cathodic) was normalized by the area of the electrodes and plotted versus scan rate (V s⁻¹) to obtain the double layer capacitance. Impedance experiments were performed at the open circuit potential (0.16 V vs. Ag/AgCl for bamboo) using the Fe(CN)₆⁴⁻/⁻ redox probe; the perturbation voltage was 10 mV in the frequency range from 0.1 to 10⁵ Hz.

Construction of the bamboo-based microfluidic heater systems

For the internal heating experiments, both faces of the bamboo were coated with the silver ink. Then, N₂ at 1 bar was forced to flow through the bamboo microchannel for 30 min, before the ink was completely dry. Next, two folded aluminum foil strips were attached at each side of the sample as described for the bamboo-based electrochemical cells. The strips were then connected to an AC power source (MPM-3503 Minipa, SP, Brazil) and a syringe pump was used to force deionized water to flow through the bamboo microchannels. A thermocouple (type K) connected to a digital thermometer was placed 1 cm downstream of the bamboo sample for the temperature measurements. For the external heating experiments, the bamboo specimen (Ø = 6 mm and L = 20 mm) was prepared as described above.

Results and discussion

Fabrication of highly conductive bamboo microchannels

Bamboo (Dendrocalamus giganteus) was selected as a raw biotemplate for the fabrication of 3D functional devices due to its enormous advantages. Compared to trees, which are used to obtain wooden materials, bamboo grows much faster, leading to higher biomass harvesting yields (kg m⁻²). Moreover, it is a low-cost, flexible, cellulose-rich, and lightweight material, which makes it an excellent choice for sustainable technologies. Its biological vascular bundle system with lined-up straight channels (Fig. 1a, xylem vessels of transportation tissue) with variable internal diameter from 50 to 200 µm boosts high-speed fluid dynamics, which is the main reason for its outstanding rapid and reproducible rates. Fig. 1a shows an optical microscopy image of a transversal cut of a bamboo culm with its living cells (parenchyma tissue) and vascular bundles (phloem and metaxylem) isolated from each other by crystalline cellulose fibers (sclerenchyma tissue). Most of the nanocoating or chemical functionalization procedures have been carried out on the external surface of bamboo to make it magnetic, ...
superhydrophobic,
self-cleaning,
conductive,
and bioresistant against fungi. To date, only our previous reports demonstrated a regioselective coating of bamboo’s metaxylem vessels with antifungal organic-capped silver nanoparticles (AgNPs) and catalytic copper ions (Cu\(^{2+}/Cu^{+}\)).

To obtain highly conductive hollow channels, we flowed commercial silver ink inside a microchannel array using a vacuum pump and removed the excess solvent by flowing N\(_2\) in the following step, as illustrated in Fig. 1b. This process results in a silver coating of microchannels, covering the pit surface of internal walls, as shown in scanning electron microscopy (SEM) images before and after metal deposition (Fig. 1c and d). A microchannel array SEM image and its respective Ag mapping using energy dispersive X-ray spectroscopy (EDS) are presented in Fig. 1e and f, respectively, confirming the internal silver ink coating. Fig. 1g and h show the X-ray microtomography (\(\mu\)CT) 3D images of the same bamboo bio-template specimen before and after silver coating. \(\mu\)CT images clearly show that microchannels are hollow throughout their entire length and silver coatings (white contrast) are only formed on inner walls along the entire length of microchannels.

The thickness of the Ag-coating on microchannels was found to be 10.3 ± 2.2 \(\mu\)m, as shown in Fig. S3.† The internal structure of bamboo is the key feature that enables built-in conductive hollow channels due to the presence of highly oriented centimeter-long microchannels. Moreover, such microarrays are very difficult to fabricate using conventional microfabrication techniques. Thus, the bamboo bio-template offers a unique platform for the fabrication of electronic, microfluidic and electrochemical devices. Additional characterization (SEM images, porosity and density values) of bamboo and Ag-coated bamboo can be found in the ESI (Table S1 and Fig. S4†).

**Anisotropic conductivity and patterning of the 3D electrical devices**

Due to the highly anisotropic architecture of bamboo’s internal structure, the electrical conductivity of the modified material has also been shown to be extremely anisotropic, as demonstrated in the schematic in Fig. 2a. The Ag-coated bamboo template (\(\Omega = 6 \text{ mm} \) and \(L = 20 \text{ mm}\)) is very conductive along the direction of the microchannels while it is highly resistive in
the direction perpendicular to them. The microchannel conductivity is $9.3 \pm 4.0 \times 10^5 \text{ S m}^{-1} (\sigma_1)$, which is the highest value reported so far for cellulose-based ordered materials. Along the direction of the channels, the electrical resistance between the top and bottom surfaces reaches its minimum values of $R_1 \sim 20 \Omega$. On the other hand, electrical resistance increases by a $10^6$ order of magnitude when the measurements are performed orthogonally to the lateral surfaces ($R_\perp > 20 \text{ M}\Omega$). Another important feature of these highly conductive structures is that there is no short circuit due to the insulator parenchyma tissue between microchannels and the absence of silver connecting parallel channels. To find out if there is any possible influence from the lignocellulose support, we measured the conductivity of the silver track ($0.2 \times 3.0 \text{ cm} \times L$) patterned on a glass slide substrate without significant alteration of the conductivity. There are some other materials that have a superior conductivity; however, the patterning routes used to prepare such materials are not compatible with the bamboo biotemplate structure (Table S2†). When compared to other work listed in Table S2† the proposed cost-effective method allows selective introduction of commercial conductive ink into the microarray vascular bundles. This new feature is only possible due to the hollow nature of the Ag-coated microchannels and it will be shown later on. Thus, our method surpasses the current state-of-the-art methods in three aspects: (i) high conductivity, (ii) possibility to create greener and sustainable functional devices that take advantage of the hollow nature of the microchannels, and (iii) scalability of production of the bamboo-based bio-devices.

Fabrication of many functional 3D electrical devices is enabled by the high anisotropy of the bamboo template together with individually electrically addressable microchannels. Fig. 2b
shows an example of an electronic circuit in which electric current flows from the bottom face of bamboo through a microchannel array to the top, lights up an LED, and then returns through another microchannel array to the bottom. The lateral surface of the Ag-coated bamboo is not conductive. However, the conductive microchannels can be assessed through the lateral surface by performing small cuts, as illustrated in Fig. 2c. For this system, the electric current 3D pathway now starts from the bottom surface, lights up the LED on the lateral wall, and then reaches the end of the circuit at the top. Fig. 2d shows an even more complex 3D electronic design in which a serpentine-like circuit was fabricated using specific regions of the top, bottom, internal and lateral surfaces of bamboo. In Fig. 2e, a system is shown which combines two pieces of conductive bamboo. One of them can be rotated around a vertical axis to light up different LEDs circuited along the external surface of the second bamboo specimen (Fig. S5†). At the bottom of bamboo (i) illustrated in Fig. 2e a triangular area was patterned with silver ink. The top surface of bamboo (ii) contains three independent circuits that can be activated when the silver contact pads of both pieces perfectly match during rotary stepwise movement. Photos illustrated in Fig. 2e (iii–vi) show the OFF and ON states.

**Microfluidic bamboo-based microfluidic heater**

Fabrication of 3D arrays of microchannels like those built on PDMS-based devices is time consuming and the layered patterning process limits the final 3D architecture. Recent advances in 3D printing have enabled the fabrication of fluidic arrays with remarkable features. However, bamboo represents a unique raw and sustainable bio-template for microfluidic applications. For instance, centimeter-long highly oriented arrays of microchannels (from 20 to 50 cm), naturally found in a full extension bamboo culm between two internodes, are difficult to fabricate by most 3D printing or other microfabrication processes. One of the main advantages of hollow conductive microchannel arrays, such as those built in the bamboo template, is the possibility to flow liquids through their microchannels. This architecture can be potentially explored on microfluidic (electro)chemical reactions to either boost the kinetics of chemical transformations or to increase the fluid temperature through the Joule effect. As a proof of concept, we fabricated a fluidic microheater to efficiently transfer heat to water that is flowing inside the bamboo metaxileme vessels. Fig. 3a shows a picture of the Ag-coated bamboo where all hollow microchannels were short-circuited. Tuning the electric current that flows through the microchannels allowed the temperature of bamboo to be increased due to the Joule heating effect, as illustrated through infrared thermography (IRT) images (Fig. 3b–d).

The temperature distribution shown through IRT images is fairly homogeneous on bamboo specimens as a result of the uniform metal coating distribution in its microchannel array architecture. To show the potentiality of the hollow-conductive fluidic bamboo-based microfluidic heater and its processes, the bamboo template was used to fabricate a microheater. Fig. 3a shows a photo of a multi-channel bamboo-based microheater (@ 6 mm and L = 20 mm) with electric contact; (b–d) infrared thermographic images of bamboo at different currents (0.5–1.5 A); (e) outlet water temperature vs. time at a fixed current and flow rate. Inset (i) shows an optical microscopy image of the Ag-coated bamboo surface presenting open channels (the scale bar is 1 mm); (f) outlet water temperature as a function of flow rate and different applied currents; (g) Joule heating efficiency with the internal and external conductive walls of bamboo.
bamboo as an integrated microfluidic heater, we flowed water into the system and measured the temperature of the water flowing out with an external thermocouple, as schematically shown in the inset image in Fig. 3e. A constant water temperature is reached after 4 minutes for all the conditions studied here but not presented ($Q_{\text{H2O}} = 0.25$–0.85 mL min$^{-1}$, and $I = 0.5$–1.5 A). Fig. 3e also illustrates the water entrance face of bamboo fully covered with Ag and open microchannels. Fig. 3f shows the steady-state water outlet temperature for different flow rates at different values of electric current. As expected, applying higher electric currents resulted in an increase of water outlet temperature for a fixed flow rate. On the other hand, the increase of flow rate resulted in a decrease of water outlet temperature, since now a greater mass of water flows through the channels with the same amount of supplied power. Thus, the water outlet temperature could be set from 25 to 55 °C by controlling either the flow rate or the electric current. This temperature range finds suitable applications in a significant number of organic reactions in flow mode. Even if the anisotropic thermal conductivity is an interesting and useful feature in many applications, our modified bamboo microheater device has the main objective of warming up water that is flowing inside the Ag-coated microchannels.

Energy efficiencies (EEs) for two different microheater setups were determined to highlight the unique advantages of an inner Ag-coated bamboo system and their results are shown in Fig. 3g. The stability of the channels against water and equations used to calculate EE (eqn (S1)–(S5)) are presented in the ESL.† In one case, electricity flows through the inner conductive hollow microchannels of bamboo (internal heating), while in the other case electric current flows on the outer bamboo Ag-coated surface (external heating). For both setups, higher flow rates resulted in higher energy efficiency values.

By increasing the flow rate we also increased the forced convection of the fluid, which results in a higher heating transfer coefficient and subsequently a higher heat flow rate between the heating source and water. For the highest flow rate values, the internal heating system achieved an EE of 55%, which is significantly higher compared to the 30% observed for the external heating system. These differences in EE are explained by low values of lignocellulosic material thermal conductivity. For the external heating system, bamboo poses higher resistance to deliver energy to heat up water inside microchannels and faster dispersion of heat to the external environment.

Fully integrated bamboo-based electrochemical cells (BECs)
A schematic of the fabrication steps of carbon-based electrodes using conductive hollow channels, epoxy resin, and carbon black paste is shown in Fig. 4a. The first step consists of spreading epoxy resin in one of the bamboo faces. Epoxy resin fully covers the bamboo face and clogs the exit of the hollow conductive channels. Before resin curing, nitrogen gas was flowed through bamboo channels to unclog the channels and preserve the epoxy resin coating on parenchyma and sclerenchyma structures, as illustrated in Fig. 4a. We kept the gas flowing through the channels until the complete cure of the epoxy resin. Unclogged microchannels were filled with carbon black nanostructures to fabricate carbon-based microelectrodes, on which each channel acts as an individual electrode. Carbon black nanostructures combined with mineral oil make the electrode surfaces hydrophobic enough to prevent the permeation of the supporting electrolyte through the silver coating inside the channel. Likewise, the epoxy resin coating prevents the wetting of bamboo and penetration of the electrolyte solution from the lateral and bottom faces of the electrode, as illustrated in Fig. S6.† Fig. 4b shows a stereomicroscope image of the bamboo top face showing a uniform coating of epoxy resin around the apertures of microchannels, which are filled with carbon black paste. Fig. 4c and d show SEM images of one microelectrode surface at low and high magnification, respectively. Mineral oil works as a binder for carbon black nanoparticles forming globular aggregates (~500 nm), as illustrated in the higher magnification SEM image (Fig. 4d). A globular morphology is commonly observed for other carbon black conductive surfaces, and the size of aggregates can vary significantly.

The electrochemical performance of the bamboo working electrode (BWE) was investigated using a 5 mM Fe(CN)$_6^{3–/4–}$ redox probe in 0.5 M KCl solution. The cyclic voltammogram obtained using the entire face of the BWE is presented in Fig. 4e. The peak-to-peak separation obtained from the cyclic voltammogram was 140 mV, suggesting a quasi-reversible redox process. This value is close to those of other high-performance electrodes obtained on cellulose-based substrates. Peak currents obtained at different scan rates revealed that the redox process on this electrode is diffusion dependent, as illustrated in Fig. 4f. This result indicates that redox species are not being trapped on the surface, indicating that nanostructured carbon surfaces do not present surface recesses that trap the redox mediator.

Since sets of conductive hollow microchannels of bamboo can be individually addressed, we demonstrated here for the first time a fully integrated electrochemical cell built in a bamboo bio-template. Fig. 4g(i) shows a schematic illustration of the BEC. Fig. S1 and S2† show the complete fabrication process and the gap between electrodes in the fully integrated cell, respectively. On the top face, illustrated in Fig. 4g(ii), silver ink was patterned and chemically oxidized to form the Ag/AgCl reference electrode. The areas corresponding to the working, reference and counter electrodes are established by the delimited area of the contact pads on the opposite face of bamboo, as illustrated in Fig. 4g(iii), S1 and S2.† This setup is possible only due to the unique architecture of the bamboo bio-template with highly oriented and isolated hollow channels, as illustrated in Fig. 1g–i. Results of electrochemical impedance spectroscopy and double-layer capacitance experiments shown in Fig. S7† confirmed the quality of the electrodes. Moreover, one main advantage of carbon paste electrodes is its suitability through modification processes. For instance, redox mediators, nanocatalysts, nanoparticles and biomolecules can be simply mixed with the conductive material and mineral oil paste. In this work, carbon paste was modified with Prussian blue (PB),
a well-known redox mediator with electrocatalytic properties toward hydrogen peroxide.  

Fig. 4h shows the cyclic voltammogram obtained using the BEC with PB modified carbon paste. As can be noticed, two redox couples are present in the voltammogram and they can be ascribed to Prussian white/Prussian blue at 0.1 V and PB/Berlin green at 0.8 V vs. Ag/AgCl redox couples. The redox couple with a formal potential of ~0.1 V is responsible for the electrocatalytic properties of the PB-based electrodes. Fig. 4i shows the cyclic voltammograms in the presence and absence of hydrogen peroxide (5 mM). As can be observed, electrocatalytic current largely increases in a potential range that is highly interesting for several electrochemical applications, analytical detection and sensor applications.

Conclusions

For the first time, ultra-highly electrically conductive hollow microchannels built in a bamboo bio-template were developed that enabled fabrication of several electronic, microfluidic and electrochemical devices. Arrays of oriented bamboo vascular bundles were coated with silver ink using a simple and low-cost vacuum-assisted method that ultimately resulted in the preparation of unprecedented ultra-highly conductive hollow microchannels. The unique anatomical structure of bamboo coupled with the anisotropic conductive coating of its microchannels led to the fabrication of complex three-dimensional electronic circuits that explored the internal, top, bottom and lateral faces of the bamboo-based biodevices. Moreover, since the hollow vascular structure of bamboo is preserved, it is possible to flow liquids through the conductive array of microfluidic channels. A self-incorporated microfluidic heater was developed to circumvent the low thermal conductivity of lignocellulosic materials. For instance, the internal Joule heating generated by these hollow conductive channels showed higher efficiencies when compared to heating performed at the bamboo external walls. The microfluidic device with an integrated thermoelectric microheater device has been demonstrated to have significant potential applications in flow chemistry among others where fluid heating is necessary. Moreover, the bamboo-based fully integrated electrochemical devices showed excellent electrocatalytic properties for portable applications due to their miniaturization. Our work paves the way toward development of greener sustainable “bambootronics” technology, where
functional electronic and electrochemical bio-devices are fabricated and integrated to explore the unique fluidic dynamics and electrical anisotropy of functionalized bamboo microchannels.

Conflicts of interest

There are no conflicts to declare.

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