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High Performance, Low Cost Carbon Nanotube Yarn based 3D Printed Electrodes Compatible with a Conventional Screen Printed Electrode System

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Abstract

3D printing technology has been widely used as a rapid prototyping fabrication tool in several fields, including electrochemistry. In this work, we incorporate 3D printing technology with carbon nanotube yarns for electrochemical sensing of dopamine in the presence of ascorbic acid and uric acid. The novel 3D printed electrode provides a circular concavity detection zone with grooves to insert three electrodes. The electrode connections are fully compatible with conventional screen printed electrode workstation setups. The CNT yarn 3D printed electrode showed excellent electrocatalytic activity for the redox reaction of dopamine (DA) in the presence of ascorbic acid (AA) and uric acid (UA). Three well-defined sharp and fully resolved anodic peaks were found with the peak potentials using cyclic voltammetry (CV) at 50 mV, 305 mV, and 545 mV for AA, DA, and UA respectively and using differential pulse voltammetry (DPV) at 91 mV, 389 mV, and 569 mV, respectively. DA detection limit was 0.87 ± 0.09 μM. The CNT yarn 3D printed electrode displayed high reproducibility and stability. The electrode design enables the study of electrode reactions at the sidewall of CNTs, which cannot be performed using electrodes made by conventional fabrication methods. The new fabrication method provides a new platform to prototype new electrode materials for electrochemistry, providing a low-cost, customizable design compatible existing screen printed electrodes technology.

Keywords

3D Printing; CNT yarn; Dopamine; Ascorbic acid; Uric Acid; voltammetry

I. Introduction

The recent development of 3D printing based rapid prototyping has led to a consumer-oriented availability of many desktop or bench-top printing devices.[1] The 3D printing process allows 3D objects to be fabricated in a bottom-up, additive fashion directly from digital designs, with no milling or molding.[2] This progress, often described as a revolution in the manufacturing industry, enables the cost-effective use of self-developed and individually designed labware and devices in the bio-science field.[3], [4] 3D printing approaches are increasingly used in several scientific and medical applications, such as tissue-growth scaffolds,[5], [6] microvascular systems,[7] orthopedic implants,[8] rehabilitation aid tools,[9] electronic device,[10] and chemical reactors.[11]

Electrochemistry is another branch of science that can benefit from 3D-printing technologies, paving the way for both design and fabrication of cheaper, higher performing, and customizable electrochemical devices.[12], [13] The ability to easily made new designs will enable 3D printing to be used to move away from the commonly used electrodes and cells for various materials. Recently, we reported a 3D printed mold for batch fabrication of carbon fiber microelectrodes (CFMEs) using polyimide resin as sealing agent. 3D printing provides an easy way to reproducibly fabricate molds, and the produced electrodes can be customized according to experimental needs with various materials.[14]

Carbon nanomaterials, such as graphene or carbon nanotubes (CNTs), are commonly used for electrochemical detection of biomolecules because of their promising electron transfer kinetics, high conductivity, good antifouling properties, and biocompatibility.[15] Screen printed electrode (SPE) fabrication method is one of the easiest approaches to apply carbon nanomaterials for electrochemical applications.[16]–[20] However, an ink needs to be made with CNT, which requires a surfactant to improve carbon nanomaterial dispersion and mineral binders or insulating polymers to improve the adhesion onto the substrate. The exact ink formulation and composition are usually patented by companies and not disclosed to the users. Moreover, the SPE fabrication method is not suitable for macrostructured materials, such as fibers. Therefore, the application of novel carbon nanomaterials using SPE fabrication method has limited choices of materials. The spacing of the connector for an SPE electrode is standard for each company and can be easily measured and then reproduced in a 3D printed mold. Here, we designed a 3D printed electrode with a connector compatible with SPE workstations, that can incorporate fiber and metal wire microelectrodes.

CNT yarns are a macrostructure of CNTs fabricated by solid state processes, and no dispersion in surfactant is required.[21], [22] Compared to graphene and CNTs paste, CNT yarns have higher purity.[23] Moreover, in comparison to randomly distributed and tangled CNTs produced by dip coating or screen printing, well-aligned CNT yarns have the advantages of high electroactivity, chemical stability, high conductivity, controllable size, and promising anti-fouling properties.[15],[24],[25] The CNT yarn has intrinsically abundant adsorption sites for neurotransmitters, such as dopamine, and has already been used for sensitive electrochemical sensing.[26],[27] Moreover, most sensor designs are based on maximizing exposure of edge plane defects which are on the end of CNT yarn.[28] Some have argued that CNT sidewalls are also electrocatalytic for dopamine, but a practical sensor that employs just the CNT yarn sidewall has not been developed.[28]–[31] Thus, there is a dichotomy between the practical and the fundamental science, and the 3D printed electrode CNT yarn electrode is a new method to fabricate a CNT sensor with only the yarn sidewalls exposed. This design will help elucidates the extent to which CNT sidewalls provide a good substrate for electrocatalytic detection of dopamine. The electrode fabrication method using 3D printing provides a low-cost device designed to work with micro-volumes of sample, and a novel approach for the application and fundamental electrochemistry study of various fiber materials.

II. Methods

A. Reagents and Materials

Dopamine hydrochloride, uric acid, and ascorbic acid were purchased from Sigma–Aldrich (St. Louis, MO). Dopamine stock solutions with concentration of 10 mM, uric acid and ascorbic acid stock solutions with concentration of 100 mM were prepared in $HClO_4$, and were diluted daily to the desired concentration in phosphate buffered saline (131.3 mM NaCl, 3.00 mM KCl, 10 mM NaH_2PO_4, 1.2 mM $MgCl_2$, 2.0 mM Na_2SO_4, and 1.2 mM $CaCl_2$ with the pH adjusted to 7.4).

B. Electrode Fabrication

Molds were designed in Autodesk Inventor Professional 2014 Student Edition, converted to an .STL file, and subsequently printed by the Department of Mechanical Engineering at University of Virginia. The 3D printed polymer molds were manufactured on a Stratasys Connex 500 Model 1 Poly-Jet 3D printer (Stratasys Ltd, MN), which has 8 print heads with 96 nozzles per head. Water jets were used to remove the support. Rigid opaque black material (VeroBlackPlus RGD875, mainly acrylonitrile butadiene styrene, Stratasys) was used because of its suitability for rapid tooling with dimensional stability and fine detail. The heads heat up to 60 °C, and the Z axis resolution with this material was 30 μm. A piece of commercially available carbon nanotube yarn (CNT yarn, 10–25 μm in diameter, 1–2 cm long, General Nano, LLC, Cincinnati, OH) was used as working electrode. The homemade reference electrode was a silver/silver chloride electrode with diameter of 250 μm, fabricated by applying 2 V potential to a 4 cm long silver wire for 30 seconds in concentrated hydrochloric acid. The counter electrode is a ~2 cm long silver wire (ESPI Metals, Ashland, OR) with a diameter of 250 μm. Electrodes materials were sealed with 5 min epoxy Loctite (Henkel Corporation, Westlake OH) which was allowed to fully cure for 24 h. The connection between electrode material and SPE adapter is achieved by stainless steel plates, and silver/silver chloride paste (The Gwent Group, United Kingdom) is used to ensure the conductivity between the plates and electrode materials.

C. Apparatus

All electrochemical measurements were performed on a Gamry electrochemical workstation (Gamry Reference 600, Gamry Instruments, USA). Cyclic voltammetry was applied with a triangle waveform of −0.2 – 0.6 V, with a scan rate of 200 mV/s. Differential pulse voltammetry was applied from 0 to 0.6 V, with amplitude of 0.05 V, pulse width of 0.05 s, sample width of 0.02 s and pulse period of 0.5 s. A commercial universal screen printed electrode cable connector (Metrohm USA Inc, FL) is used to connect the electrochemical workstation and the 3D printed electrodes. Scanning electron microscope (SEM) images were taken on Merlin field emission SEM (Zeiss, Thornwood, NY) with a secondary electron detector using an accelerating voltage of 2 kV and a working distance of 5.0 mm.

III. Results and Discussion

A. CNT Yarn based 3D Printed Electrode Fabrication

Fig. 1A shows the design of a 3D printed electrode, with the dimensions of 30 mm × 10 mm × 2mm. Briefly, the design is three grooves to place the working, reference and counter electrodes in the 3D printed electrode substrate. The detection zone is a circular concavity that can hold a drop of solution (~50 μL) across the three electrodes. Three metal plates are used to connect the electrodes to a potentiostat via a SPE adapter cable.

As shown in Fig. 1B, the three grooves are for silver counter electrode (500 μm in diameter), CNT yarn working electrode (250 μm in diameter), and Ag/AgCl reference electrodes (250 μm in diameter) from bottom to top, respectively. Epoxy resin is applied as sealing agent to fix electrode materials in the grooves and limit the area of detection zone after placing all the three electrodes in grooves. Moreover, the intrinsically hydrophobic property of epoxy sealing would also help restrict the sample solution in the 4 mm diameter (0.6 mm deep) circular concavity detection area. The distance between working and reference electrodes (300 μm) is half of the distance between working and counter electrodes (600 μm), to reduce the ohmic drop. The connections between three electrodes to SPE adapters are achieved by stainless steel plates with width of 2 mm placed in the grooves with the spacing between each plates of 0.8 mm (Fig. 1B). While this electrode was designed to fit a Metrohm universal screen printed electrode cable, 3D printed molds could be easily revised to fit the adapters for different brands of widely used and commercially available SPEs from Pine Instrumentation Inc., DropSens, or CH Instruments.

The 3D-printed electrode substrate is primarily made of acrylonitrile butadiene styrene (ABS), which is not soluble in aqueous solutions. With the help of water jets, 30 μm resolution is achieved by using ABS, which is suitable for our design with channels of hundreds of microns wide. The average cost of materials including ABS, epoxy, and electrode materials is less than 1 dollar per electrode. More importantly, the 3D printed electrode design allows any materials that are fiber-like to be made into an electrode e.g. carbon fiber, CNT yarn/fiber, metal or polymer fibers. These materials would not be easy to use with traditional SPE, so this mold helping broadens the materials that can be tested.

B. Electrochemical Characterization

In this work, a CNT yarn is used as working electrode material. CNT yarn is a macrostructure of CNTs with well-aligned multiwall CNTs (MWCNTs) bundles spun through the yarn, as shown in Fig. 1C. The continuous MWCNTs with diameter about 30 – 50 nm (Fig. 1D) have abundant sp^2 hybridized carbons compared to sp^3 hybridized carbons which are mainly located at the ends of CNT bundles. The 3D printed electrode using CNT yarn as working electrode was electrochemically characterized using cyclic voltammetry scanning from −0.2 to 0.6V and back at 200 mV/s. The response to 300 μM dopamine (DA, red curve) is shown in Fig. 2A For DA, the cathodic and anodic peaks appear at about 280 mV and 330 mV, respectively, a substantial positive shift of the oxidation peak potential compared to other carbon nanomaterials.[16], [32] The separation between the oxidation and

reduction peak potential (ΔE_p) is 53 ± 2 mV (n=4 electrode), which is smaller than several previous works using CNT-based SPEs,[16], [32] indicating faster electron transfer kinetics.

Ascorbic acid (AA) and uric acid (UA) are common interferences in tissue,[15] and the DA selectivity over AA and UA were tested at CNT yarn 3D printed electrodes. Fig. 2A(b) shows the CV of a mixture of 300 μM DA, 1 mM AA, and 1 mM UA (black curve) at the CNT yarn 3D printed electrode. The CV has three well-defined sharp, and fully resolved anodic peaks at 50 mV, 305 mV and 545 mV, corresponding to the oxidation of AA, DA, and UA, respectively. The calculated oxidation peak potential separations are 255 mV for AA–DA, 240 mV for DA–UA, and 495 mV for UA–AA, demonstrating promising selectivity for simultaneous determination of these three species. Fig. 2B displays differential pulse voltammogram (DPV) obtained at the CNT yarn 3D printed electrode for a mixture containing 300 μM DA, 1 mM AA, and 1 mM UA. The potentials for AA, DA, and UA are at 91 mV, 389 mV, and 569 mV, respectively, and the separations for AA-DA, DA-UA, and AA-UA are 298 mV, 180 mV, and 478 mV, respectively. Thus, the CNT yarn 3D printed electrode can distinguish DA, UA, and AA using both CV and DPV.

CNT yarn 3D printed electrodes were used to detect different concentrations from 50 μM to 500 μM DA using CV and the plot of oxidation current versus concentration is shown in Fig. 2C (n = 4). A linear response was obtained from 50 μM to 400 μM (R^2 = 0.9817), and the limit of detection (LOD) is 0.87 ± 0.09 μM (S/N = 3). To assess the stability of the electrodes, the dopamine CV peak current was measured once per day for 4 days (Fig. 2D). The calculated RSD is only 0.986%, indicating promising shelf stability as well as its low susceptibility to electrode fouling caused by oxidized products that could strongly absorb onto the electrode surface.[33], [34] The electrode-to-electrode reproducibility was also checked by comparing four CNT yarn 3D printed electrodes prepared under the same conditions. The RSD for dopamine was 4.12%, confirming that the fabrication method is highly reproducible.

Since most of the CNT yarn studies have only investigated the electrochemical performance at its polished tip, the electroactivity of the sidewall of CNT yarn is not well understood.[27], [35] For example, the redox reaction of dopamine depends on the surface oxygen-containing functional groups, surface roughness, and **π**–**π** stacking reversibility.[15], [36]–[40] In contrast to most sensor designs, which are based on maximizing exposure of edge plane defects which are on the end of CNT yarn[28], the novel 3D printing assisted fabrication method provides a platform for the electrochemistry study of the reactivity of CNT sidewalls. The kinetics of electrode reaction were investigated by evaluating the effect of CV scan rate on the DA oxidation and reduction peak currents (Fig. 2E). Both the anodic and cathodic peak currents were proportional to scan rate in the range of 50 to 500mV/s (Fig. 2F). The linear regression equation for the anodic peak current was $I_{p,a}$ (μA) = 2.33 + 0.21*v (mV/s), with a correlation coefficient of R^2 = 0.9999, and for the cathodic peak current was $I_{p,c}$ = −2.74 – 0.18*v (mV/s), with R^2 = 0.9999. Both DA oxidation and reduction reactions at CNT yarn 3D printed electrodes are adsorption controlled processes, similar to DA redox reaction at the tips of CNT yarn and carbon fiber microelectrodes.[27], [34], [35] The adsorption mechanism of DA reaction on CNTs and carbon fiber is due to the electrostatic interaction with the negatively charged oxygen-containing functional groups

under physiological pH.[25], [41], [42] But due to the lack of sp^3 hybridized carbons on the pristine CNT yarn sidewall, the $\pi - \pi$ stacking between dopamine and CNTs sidewall is likely to play an important role for the adsorption controlled process.

A secondary oxidation peak at 160 mV was observed for dopamine with CV, especially at slower scan rate (Fig. 2E, black arrow). The secondary oxidation is likely due to the oxidation of leucodopaminechrome (LDAC) to dopaminechrome (DAC), in the synthetic pathway of DA $\rightleftharpoons$ DOQ $\rightharpoonup$ LDAC $\rightleftharpoons$ DAC. Similar results have been observed at a long-length (hundred micrometers) CNT electrodes,[43] but not at other carbon electrodes such as carbon paste, graphene, fullerene, nanofiber, and graphite.

The 3D printed electrode method provides a much easier fabrication approach than dispersing and coating long-length CNTs on a substrate made and therefore is a good platform to perform further fundamental electrochemical studies of CNT sidewall reactivity. Overall, the 3D printed electrode fabrication method provides a platform for testing the electrochemical reactivity of any fiber or wire electrode material with ease. The design has revealed interesting good electrocatalytic properties of CNT yarn sidewalls and enhancement of side reactions from cyclization products that are stabilized at the CNTs.

IV. Conclusions

In this work, we investigate a novel 3D printed platform for electrode fabrication that expands the electrochemical application of various fiber materials. The new fabrication method has the advantages of low-cost, customizable design, and high reproducibility. Moreover, the compatibility to existing SPE electrochemistry workstations minimizes the cost because no extra device/instrument is required. A CNT yarn was used as the electrode material. The LOD for DA with CV is less than 1 μM. The CNT yarn electrode demonstrated promising selectivity of DA in the presence of AA and UA, enabling simultaneous detection with CV or DPV. In addition, the good sensitivity and adsorption controlled process for DA demonstrates possible electroactivity of CNTs sidewalls, and indicates the 3D printed electrode method is a good platform for electrochemistry studies on sidewalls which are hard to study with conventional fabrication approaches. Future studies could examine the surface properties and electrochemical performance after pretreatments such as surface modifications or decorated with polymers, metals particle, or biomaterials because the CNT yarn sidewall is a highly homogenous structure for sensing.[44], [45] The new 3D printed platform allows broad application of not only CNT yarn but also other materials such as metal or polymer fibers. 3D printed platforms could also potentially be applied as electrode arrays, which would allow the calibration and the analysis of several analytes simultaneously.

Acknowledgments

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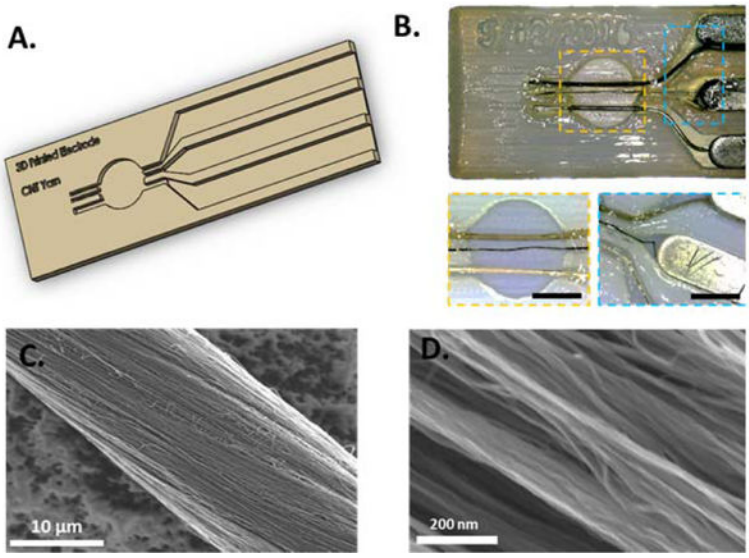

Fig. 1.

Illustration of electrode design and CNT yarn 3D Printed Electrode. (A) Design of the 3D printed electrode substrate for CNT yarn. (B) Image of the CNT yarn 3D printed electrode top-view. Circles shows zoom-in images of the detection area and electrode material-metal plate connections. Scale bar: 2 mm. From top to bottom, the electrodes are a Ag/AgCl reference electrode, CNT yarn working electrode, and silver counter electrode. (C) SEM Image of a CNT yarn with spun well aligned CNT bundles and (D) zoomed in SEM image on the same CNT yarn sample.

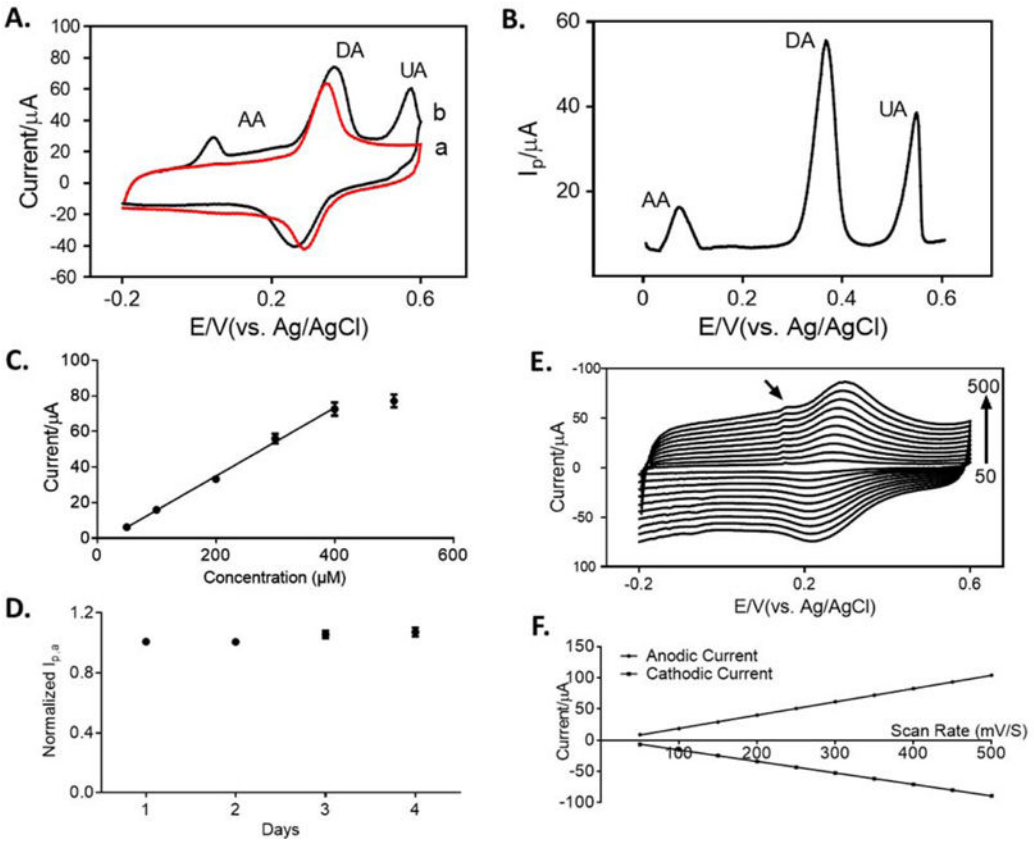

Fig. 2.

Electrochemical characterization of CNT yarn 3D printed electrodes. (A) Cyclic voltammogram of 300 μM dopamine PBS (pH 7.4) solution (curve a) and a mixture of 300 μM dopamine, 1 mM uric acid and 1 mM ascorbic acid solution (curve b). Scan rate 200 mV/s. (B) DPV of 300 μM dopamine in the presence of 1 mM uric acid and 1 mM ascorbic acid. (C) Anodic current to different concentrations of dopamine in a range of 50 to 500 μM (n = 4), with scan rate of 200 mV/s from −0.2 to 0.6 V. A linear range from 50 to 400 μM has R^2 of 0.9817. (D) The stability experiment was performed by testing the response of CNT yarn 3D printed electrodes (n = 4) to 300 μM dopamine every day for four days, with scan rate of 200 mV/s from −0.2 to 0.6 V. (E) Cyclic voltammogram of 50 μM dopamine at different scan rates from 50 to 500 mV/s, and (F) the relations between the anodic/cathodic peak current and scan rate.