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Patternable Nanowire Sensors for Electrochemical Recording of Dopamine

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Abstract

Spatially resolved electrochemical recording of neurochemicals is challenging due to the challenges associated with producing nanometer scale patternable and integrated sensors. We describe the lithographic fabrication and characterization of patternable gold nanowire (NW) based sensors for the electrochemical recording of dopamine (DA). We demonstrate a straightforward NW-size-independent approach to align contact pads to NWs. Sensors, with NW widths as small as 30 nm, exhibited: considerable insensitivity to scan rates during cyclic voltammetry, a nonlinear increase in oxidation current with increasing NW width, and the selectivity to measure sub-maximal synaptic concentrations of DA in the presence of interfering ascorbic acid. The electrochemical sensitivity of gold NW electrode sensors was much larger than gold thin film electrodes. In chronoamperometric measurements, the NW sensors were found to be sensitive for sub- μ M concentration of DA. Hence, the patternable NW sensors represent an attractive platform for electrochemical sensing and recording.

Keywords

patternable nanowire; dopamine; nanoelectrode; chronoamperometry; neurochemical

INTRODUCTION

Nanoelectrodes^{1, 2} can revolutionize electrochemical recording of neurochemicals³ by enabling (a) measurements with high spatial resolution, (b) steady state reactions achieved even during fast recordings,⁴ (c) low parasitic capacitance,⁴ and (d) minimal disturbance to the surrounding cells thereby minimizing homeostatic disruption during measurement. Nanoelectrodes while promising for unraveling nanoscale electrochemical processes^{1, 4, 5} also offer a possible route to measure neurotransmitter concentrations within a single 20–30 nm synapse.⁶ One dimensional nanostructures such as nanowires (NWs) and carbon nanotubes have been used for biosensing,^{7, 8} including neurochemical recording.⁹ Most neurochemical

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Supplementary Information Available Contents of supporting information

[1] SEM images of 776 $\pm$ 38 and 816 $\pm$ 40 nm nanowire (NW) sensors.

[2] Dopamine (DA) oxidation current vs. concentration for the 1040 $\pm$ 457 nm NW sensor.

[3] Dopamine (DA) oxidation current vs. concentration showing sub- μ M level DA detection with the NW sensor.

recording studies have been carried out with NW or nanotube forests,⁵ the overall recording dimensions of the probes are several square microns. However, these sensors are especially useful in neuroscience when they are fabricated in isolation or in well-patterned arrays to enable recording with nanoscale spatial resolution. For example, in an in-vitro study, vertically aligned isolated carbon fibers were utilized to measure electrophysiological signals from brain slices¹⁰ and cultured neurons;¹¹ the smallest width of these fibers was 500 nm. Additionally, in-plane arrays of 30 nm silicon NW field effect transistors were used to stimulate, inhibit and measure neuronal signals through cultured cells;¹² no electrochemical measurements were performed. One significant hurdle in the utilization of isolated or well structured NW array based sensors is that while it is straightforward to synthesize these 1D nanostructures using electrodeposition in templates^{13, 14} or vapor-liquid-solid methods,^{15, 16} directed assembly and wafer scale integration with larger contact pads is still very challenging.^{9, 12}

In this paper, we describe the lithographic approach to produce NW electrochemical sensors and subsequently demonstrate their ability to perform electrochemical recording of DA. NW growth for our sensors is based on lithographically patterned nanowire electrodeposition (LPNE),¹⁷ as first described by *Menke et. al.*¹⁴ the attributes of LPNE are described elsewhere.¹⁸ Here, we integrated single or precisely arrayed NWs for neurochemical sensing. We synthesized and integrated NWs with widths ranging from 30 to 1000 nm and lengths from 1 to 20 mm, it is noteworthy that control over width and length of NWs has already been demonstrated elsewhere.¹⁴ In this application, the highlight of the sensor fabrication approach is that macroscale contact pads can be easily integrated with even 30 nm wide NWs using photolithography and a basic optical microscope. These NW sensors were used to measure dopamine (DA). DA is an electroactive¹⁹ and critical neurotransmitter³ enabling neuronal communication and has also been implicated in a number of neurological disorders including Parkinson's disease.

EXPERIMENTAL SECTION

Sensors were fabricated on cleaned, diced glass substrates (Corning) (Figure 1A). Glass is a good insulator and provides a low background current. A 100 nm thick nickel (Ni) film was thermally evaporated (Figure 1B) at a slow rate of approximately 0.1 nm/sec, at 10^{-5} Torr. A photolithographic step with Shipley 1805 resist was used to pattern exposed Ni regions (Figure 1C); any two dimensional shape such as a rectangle, square or circle could be defined. The exposed Ni was etched using 0.8 M HNO_3 (Figure 1D); the etching time was precisely controlled to overetch the Ni so that an undercut was formed to restrict subsequent gold NW deposition between the glass substrate and the photoresist overhang (Figure 1E). In our studies, the typical size of the photoresist overhang was 600 nm. The typical etch rates were in the range of 20 to 25 nm/min. Gold (Au) was electrodeposited using a commercial TG-25 E gold plating solution (Technic) at 0.5 mA/cm² current density (Figure 1E). It should be noted that since the exposed Ni area is very small (on the order of 10^{-4} cm²), it was necessary to introduce a larger metallic sample (0.25 cm²), in addition to the NW growth sample, at the cathode to enable an accurate estimation of the plating time and current density required to achieve a specific NW width. We found that the brief application of a 0.01 mA anodic current for 10 sec prior to NW deposition, in a TG-25 E solution resulted in smoother NWs.

In order to integrate larger contact pads, we took advantage of the fact that the NWs were several mm long and were easily visible under a basic optical microscope, as they outlined the sides of precursor Ni patterns (Figure 1F and H). It should be noted that the concept of aligning subsequently defined NWs with respect to larger clearly visible patterns is a highlight of this process. Hence, we purposefully retained the Ni seed layer for the easy alignment and to avoid NW delamination²⁰ during subsequent steps. In our experiments, photolithography was first used to define Ni contact pads atop the NWs and Ni was subsequently etched only within an

exposed region (Figure 1H). Then Au was evaporated within this region, and the photoresist was dissolved, leaving behind Au within the exposed region (Figure 1I). Any remaining Ni on the wafer was then etched. The contact pads and a part of the NWs were insulated using a UV curable transparent insulator epoxy⁹ (Norland Optical Adhesive-68) (Figure 1J). The epoxy was cured by exposure to a mercury lamp for 30 min. The sample was then heated at 50 00B0C for 10 hrs to enhance glass-epoxy adhesion. Since the NWs were several millimeters long, parts of them could be insulated, thereby ensuring that the contact pads were completely covered. In contrast, it is extremely challenging to ensure electrical insulation of contact pads connected to NWs or nanotubes that are only a few microns long.⁹ All the NWs had the same thickness of 100 nm; we fabricated NWs with various widths.

All electrochemical studies were performed in phosphate buffer saline (PBS) at a pH of 7.4. Currents below 10 nA were measured using a two terminal circuit and with a Keithley source meter (Model 6430).²¹ Cyclic voltammetry (CV) was performed using a three terminal circuit and with a Princeton Applied Research Versastat3 potentiostat. Solutions of DA (Alfa Aesar) and ascorbic acid (AA) (Sigma-Aldrich) were dissolved in DI water and were utilized within two hours. The PBS solution was purged with nitrogen gas for 5 minutes prior to and during the measurements to minimize the interference from dissolved oxygen.

RESULTS AND DISCUSSION

SEM images of representative NWs with 30 ± 5 , 214 ± 27 , 314 ± 60 , 614 ± 67 , and 1040 ± 457 nm widths; and with lengths of 1, 24.4, 5.5, 23.4, and 16.8 mm, respectively are shown in Figure 2. SEM images of 776 ± 38 and 816 ± 40 nm wide NWs, also used in this work are included in Figure S1 of the supporting information. The widths typically varied by approximately 20% along their lengths; this variation increased to 50% for the wider 1040 nm NWs, as the electroplated Au extended beyond the photoresist overhang.

We first measured the oxidation potential for DA using an electrodeposited 200 nm Au thin film electrode, and found it to be approximately 0.3 V vs. Ag/AgCl which is comparable with published literature.²² All chronoamperometric experiments were done above this value (at 0.5 V). A number of control experiments were performed to confirm that the electrochemical signals measured were obtained only from the NWs. The oxidation current measured with a 614 nm wide NW sensor for 1 mM DA, decreased by over three orders of magnitude after etching of NWs (Figure 3A–B). Here, the background current observed from the insulated metal pads was <1 nA. We then compared the electrochemical activity of exposed and covered NWs on two adjacent sensors on the same glass substrate. In this experiment, NWs of one sensor were completely covered by the insulator to electrically decouple them from electrolyte. No measurable current was observed from covered NWs while exposed NW sensors showed an increase in current on addition of 100 μ M aliquots of DA to PBS; (Figure 3C). We also measured the current from two adjacent (and exposed) NW sensors. Here, it should be noted that both NWs have the similar lengths, thicknesses and widths since they were fabricated simultaneously. The background current and DA oxidation current from two sensors were similar (Figure 3D).

It is known that a reduction in electrode size can cause electrochemical oxidation to occur under steady state conditions, even at high scan rates.²³ To study the effect of scan rates, CV studies were performed (using a platinum counter electrode and an Ag/AgCl reference electrode) with NW sensors and compared to carbon fiber (10 μ m diameter and 50 μ m long, CF10-50 WPI, Florida) and electrodeposited Au thin film (200 nm thick; 0.36 cm² exposed area) electrodes. The shape of the CV curves obtained with our NW resemble those observed previously with boron nitride nanotubes²⁴ and nanoelectrodes.¹ We observed peakless CV curves (Figure 4A); which we attribute to the enhanced mass transport^{25, 26, 27} In contrast, due to slow diffusion,

DA oxidation peaks were clearly observed on carbon fiber (Figure 4B) and thin film electrodes (Figure 4C). The CV curves for NW sensors were significantly less affected by the scan rate as compared to that of carbon fiber (Figure 4B) and thin gold film electrodes (Figure 4C). The current density at 0.3 V for 300 μ M DA at (0.1, 0.5) V/sec scan rates for the NW sensor, carbon fiber and thin film electrodes were found to be (2.21, 2.64), (0.15, 0.53), and (0.27, 0.69) mA/cm², respectively. On changing the scan rate from 0.1 to 0.5 V/sec, the current increased by a factor of 1.2, 3.5 and 2.6 for the NW, carbon fiber and thin film electrode, respectively. We also compared the oxidation current at various rates between NW and thin film electrodes; the oxidation current at various scan rates normalized to that at the slowest rate is plotted in the inset of Figure 4A. We surmise that the CV curves for NWs are also influenced by a voltage drop due to a difference in electrical resistance along the length of the NW. A detailed analysis of the CV curves for NWs incorporating both the effect of increased mass transport and increased electrical resistance along the NW length are beyond the scope of this paper.

In order to demonstrate the utility of these NW sensors for neurochemical recording, they must be sensitive enough to discern biologically relevant concentrations of DA. We envision the use of these electrodes for measurement of DA with spatial resolution on the size scale of a single synapse. It is estimated that the synaptic concentration of DA is 1.6 mM.⁶ DA concentrations were measured chronoamperometrically (CA), at a frequency of 20 Hz, with NW sensors of average widths ranging from 30 to 1040 nm. On addition of DA aliquots, in each cycle, the current first increased and then decreased (Figure 5A). The current was averaged over data points between 50–90 % of the cycle and plotted vs. DA concentration for each NW sensor (Figures 5B). Even 30 nm wide NW sensors exhibited excellent linearity. Average values obtained from experiments done in triplicate showed some variability (Figure 5C); however, linearity was only marginally affected (Figure 5B and C). We also observed that the noise increased with increasing NW length; this observation is consistent with carbon fiber electrode measurements;²⁸ and has been previously attributed to increased parasitic capacitance. For the smaller 30 nm NW sensors, since the exposed area was smaller, reliable oxidative currents could be measured only with DA doses as small as 400 μ M; nevertheless, this concentration is well below the maximal DA estimated concentration.⁶ The currents were also recorded on NWs with average widths of 214, 614 and 1040 nm and found to be linearly dependent on DA concentration. Oxidation current vs. DA concentration plot for 214 and 614 nm NW are given in Figure 5D and Figure 5E, respectively. Similar data for the NW sensor with the largest 1040 nm width is included in Figure S2 of the supplementary section. Each experiment was repeated at least three times with freshly prepared solutions. The average current measured, (per unit millimeter of NW length and per 400 μ M of DA) with 30 $\pm$ 5, 214 $\pm$ 27, 314 $\pm$ 60, 614 $\pm$ 67, and 1040 $\pm$ 457 nm wide NW sensors, was found to be 0.04 $\pm$ 0.02, 2.53 $\pm$ 0.62, 1.28 $\pm$ 1.58, 14.77 $\pm$ 2.31 and 16.24 $\pm$ 6.47 nA, respectively. Our sensor showed good linearity up to sub- μ M level DA (Data in supplementary section). A further improvement in the detection limit may be possible by further minimizing the leakage current using other insulating films with high impermeability²⁹ and low dielectric constant.⁵ The typical background current in our case, 1 nA and higher, was two orders higher than that of commercial carbon fiber electrode; with $\sim$ 0.01 nA background current carbon fiber electrode exhibited nM level detection limit. CA data obtained from multiple measurements on a specific sensor were reproducible. However, we obtained excellent linearity in fast chronoamperometric measurements; CA at 50 Hz (20 msec temporal resolution) was found to be linear. It should be noted that a large number of synaptic changes in neurotransmitter concentrations occur within these time scales^{30, 31}; hence the sensors are relevant to probe such dynamics.

We observed a nonlinear relation between DA oxidation current and NW width (Figure 5F). To enable a fair comparison, all the current values were plotted for the same concentration of DA (400 μ M) and are normalized to the NW lengths. It is noteworthy that in steady state, the 2D diffusion equations solved for a band shape ultramicroelectrode ($L \gg w \gg h$) predicts a

non-linear dependence of oxidation current on width.²³ However, since the width and thickness of our NWs are of the similar sizes, as schematically shown in the inset of Figure 5F, the elucidation of experimentally observed nonlinearity will require solving Fick's law in three dimensions;²³ with the added complication of a potential drop along the NW length.

The sensitivity of the NW sensors was compared to the sensitivity of both the carbon fiber electrodes and the electrodeposited thin films (Table 1). It is interesting to note that the electrodeposited Au NW electrodes show a higher sensitivity as compared to electrodeposited Au thin films, indicating a size and dimensionality effect. Although a variation in sensitivity was observed with NWs of different lengths, they were all at least one order of magnitude more sensitive than the Au thin film. A higher sensitivity of NW sensors is consistent with the enhanced mass transport due to the dominance of radial diffusion.^{4,5, 23} A deeper understanding of the enhanced sensitivity relation to electrode's geometry will necessitate solving Fick's diffusion in 3D,²³ which is beyond the scope of this paper. We do not have a clear explanation for the lower sensitivity for 30 nm wide NW sensors as compared to wider NWs; however we surmise that this lower sensitivity may be due to the large resistance change along the NW length, which is typically one order of magnitude larger for the 30 nm wide NWs as compared to the wider 200 nm diameter wires. This change in resistance along the NW length can significantly influence the magnitude of DA oxidation current and hence the sensitivity.

A significant challenge for in-vivo electrochemical recording is the ability to measure DA in the presence of a severe electrochemical interferent AA;^{3, 22, 32} the oxidation potential of AA is similar to that of DA (Figure 6A). However, the electrochemical behavior of both AA and DA are known to be strongly influenced by the chemical composition of the electrode surface.²³ Gold electrodes have been reported to be relatively inactive to AA,³³ to the extent that an activation step is generally needed to produce a sizeable oxidation current. We have utilized this insensitivity to AA as an advantage to enable DA specific electrochemical sensors. The oxidation current measured with 50 μ M aliquots of DA remained unchanged in the presence of 400 μ M AA. Additionally, the current measured with 50 μ M aliquots of pure AA was one order of magnitude lower than that of DA (Figure 6B). This study suggests that measurements with Au NWs may enable selective measurements of DA in the presence of AA, without any specific surface treatments. NW sensors exhibited 0.2 nA/ μ M sensitivity in the presence of 400 μ M AA. Further selectivity, if needed, can be enhanced by self-assembled monolayers²² and the use of advanced voltammetric methods.³⁴

In summary, we have produced highly sensitive patternable NW sensors for electrochemical recording of DA. We successfully produced NW sensor with NW width as small as synaptic gap. Additionally, our sensor can be precisely and conveniently patterned and arrayed, making them attractive for integration with microfluidic devices and cell culture substrates. This feature is important for both *in vitro* and *in vivo* measurements. The oxidative current increased non-linearly with increasing NW width. The Au electrodes show enhanced selectivity to DA over AA without any additional surface treatments. Additionally, the large lengths of the NWs make them potentially attractive for in-vivo recordings and possibly therapeutic deep brain stimulation.³⁵ Apart from neurochemical recording, the sensor fabrication, alignment and insulation strategies can be used to construct alternative biosensors. Since the NW widths can also be readily varied, as per LPNE method,¹⁷ this system can be used as a test bed to study the influence of electrode size on chemical sensing and related properties. As a highlight, we observed that 1D NWs produced 1–2 order more oxidation current per unit area as compared to that seen with 2D thin film electrodes. Our sensors are well suited for studying the neuron cells cultured on insulating substrate,^{12, 36} containing high density NW sensors. NW sensors within, or around, synaptic junctions can be utilized to measure DA concentration under the influence of intended stimuli. *In vitro* measurements for example, can be achieved by culturing

neurons atop the patterned NWs and directing axonal growth using nerve growth factor gradients³⁶; *in vivo* measurements can be achieved by patterning single or arrayed NWs on already existing probes. Here, concerns of NW breakage and precise positioning the NWs precisely within synaptic junctions remain; however, ease of NW integration and the ability to produce long NW sensors on robust substrates ameliorate some of these concerns. Depending on the application, sensors for *in vivo* recording may also require further optimization of the electrode surface and insulation to improve DA detection sensitivity and selectivity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Schematic diagram of the fabrication of NW based electrochemical sensors. (A–B) Ni was evaporated on a glass substrate. (C) Photolithography was used to pattern exposed regions within the Ni. (D) Ni was etched to form an undercut. (E) Au was electrodeposited. This image is a cross-sectional view along the dashed line in Figure (D). (F) The photoresist was dissolved. (G) A second layer of resist was spun and the contact pads were defined photolithographically. (H) Ni was etched and (I) Au was evaporated with a thin chromium adhesion layer. (J) The Au contact pads and parts of the NWs were insulated with an epoxy. (K–L) Optical images showing progressively zoomed-in images of insulated NW sensors.

Figure 2. SEM images of the electrically exposed sections of the NW sensors with widths of (A) 30 nm, (B) 214 nm (C) 314 nm, (D) 614 nm, and (E) 1040 nm. Figure (A) also shows the edge of the 30 nm NW and the insulation (Dark region). Figures (B–E) are shown with the same scale bar for comparison.

Figure 3.

Control experiments performed to confirm that the electrochemical signals measured were obtained only from the exposed NWs. Optical images of exposed NWs (A) before and (B) after etching. The corresponding DA oxidation currents measured in 1 mM DA, before and after etching are plotted in the inset graph in (B). (C) On the addition of 100 μM aliquots of DA, NWs covered by the epoxy insulation produced negligible current as compared to electrically exposed NWs. (D) A comparison of oxidation currents measured in 100 μM DA, per 1 mm length for two NW sensors, on the same substrate. Similar currents were obtained which show that the sensors can be fabricated with reasonably low variability.

Figure 4.

Cyclic voltammetry (CV) of (A) a 776 ± 38 nm wide NW, (B) commercial carbon fiber and (C) Au thin film electrode (thickness of 200 nm, with an exposed area of 0.36 cm^2) in $300\text{ }\mu\text{M}$ DA at voltage ramp rates ranging from 0.001 to 0.5 V/sec. The inset in (A) is the oxidation current (normalized to that at the slowest scan rate) plotted at various scan rates for the NW and the Au thin film electrode.

Figure 5.

Chronoamperometric results of DA in PBS for NW sensors with widths of (A–C) 30 nm (D) 214 nm and (E) 614 nm. For the 30 nm electrode, Figure (A) is the raw data measured on addition of 400 μM aliquots of DA; the arrow indicates the instance at which DA was added. (B) is the average current over 50–90% of each cycle for a single electrode; excellent linearity was observed. (C–E) A plot of the average current over three measurements for each of the 30 nm, 214 nm and 614 nm electrodes. (F) A plot of the average current (for μM DA and normalized to the NW lengths) vs. NW width. Also shown in the inset is the three dimensional profile of the geometry of the NW electrode.

Figure 6.

The measurement of DA in a background of AA: (A) CV of DA and AA on a 1.5 cm² gold electrode at 0.5 V/Sec. (B) A plot of the oxidative current vs varying concentrations of AA, and DA (in the presence of 400 µM AA) for a 214 nm NW sensor. The sensors are more selective to DA.

Table 1

Comparison of current density (mA/cm^2) for $100\ \mu\text{M}$ DA recorded during chronoamperometric studies at $0.5\ \text{V}$ oxidation potential vs. Ag/AgCl on an electrodeposited Au thin film, carbon fiber electrode and Au NW sensors of various widths (indicated in nm).

Sensor Type	Oxidation current (mA/cm^2)
Au thin film	0.043 ± 0.001
Carbon fiber	0.66 ± 0.01
NW ($30 \pm 5\ \text{nm}$)	0.407 ± 0.15
NW ($214 \pm 27\ \text{nm}$)	10.07 ± 2.5
NW ($614 \pm 67\ \text{nm}$)	25.87 ± 4.0
NW: ($1040 \pm 457\ \text{nm}$)	17.81 ± 7.0