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## Diazonium-Based Anchoring of PEDOT on Pt/Ir Electrodes via Diazonium Chemistry

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Conducting polymers, specifically poly (3,4-ethylenedioxythiophene) (PEDOT), have recently been coated onto Pt/Ir electrodes intended for neural applications, such as deep brain stimulation (DBS). This modification reduces impedance, increases biocompatibility, and increases electrochemically active surface area. However, direct electropolymerization of PEDOT onto a metallic surface results in physically adsorbed films that suffer from poor adhesion, precluding their use in applications requiring in vivo functionality (i.e. DBS treatment). In this work, we propose a new attachment strategy, whereby PEDOT is covalently attached to an electrode surface through an intermediate phenylthiophene layer, deposited by electrochemical reduction of a diazonium salt. Our electrodes retain their electrochemical performance after more than 1000 redox cycles, whereas physically adsorbed films begin to delaminate after only 40 cycles. Additionally, covalently attached PEDOT maintained strong adhesion even after 10 minutes of ultrasonication (vs. 10 s for physically adsorbed films), confirming its suitability for long-term implantation in the brain. The simple two-step covalent attachment strategy proposed here is particularly useful for neural applications and could also be adapted to introduce other functionalities on the conducting surface.

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The advancement of medical science and technology has tremendously improved life expectancy and quality of life. Nevertheless, the increasing prevalence of neurological diseases is a growing concern, especially considering the limited effectiveness of drug and psychotherapy treatments.<sup>1</sup> Deep brain stimulation (DBS) has shown promising results for the treatment of movement disorders, such as Parkinson's disease, dystonia, and essential tremor,<sup>2-4</sup> and it is being expanded to other types of mental illness.<sup>5,6</sup> DBS involves the stimulation of specific regions of the brain (e.g. sub-thalamus nucleus or Broadman Area 25 via electrical impulses<sup>7,8</sup> and requires permanent surgical implantation of microelectrodes.<sup>9</sup> Platinum/iridium (Pt/Ir) electrodes have become the gold standard for DBS, as they exhibit excellent electrical conductivity, mechanical strength, and long-term electrochemical stability, in addition to greater resistance to fouling compared to other materials.<sup>10-13</sup> Current efforts are focused on improving these electrodes using conducting polymer coatings such as poly (3,4-ethylenedioxythiophene) (PEDOT).<sup>14-17</sup> The addition of a PEDOT layer is expected to increase electrochemical performance (e.g. higher surface area and improved impedance), which would lead to enhanced electrical stimulation and decreased battery usage. Furthermore, the PEDOT layer serves as a soft organic interface that greatly improves the biocompatibility of the Pt/Ir electrode within the brain.<sup>13-15,17-19</sup> Unfortunately, common polymer deposition techniques such as spin coating are not well suited to microelectrodes geometries. Similarly, in the case of direct electropolymerization on metal surfaces, there are only weak physical interactions between the metallic and polymer surfaces (i.e. physisorption), which lead to rapid delamination of the PEDOT film.<sup>16,20</sup> These issues have been partially addressed through improving the adhesion of the conducting polymer coating via the addition of functional groups<sup>21</sup> or nanopatterning of the electrode surface.<sup>22-24</sup> While these approaches improve PEDOT adsorption, chemical bonding would be preferable for DBS electrodes, which must be robust and remain active for many years. Covalent modification of conducting surfaces using diazonium chemistry has

been thoroughly explored since their introduction by the Pinson research group.<sup>25-27</sup> However, the majority of this work was performed on carbon surfaces, and there has been much fewer reports of successful diazonium salt grafting on noble metals.<sup>28-30</sup> Herein, we propose the covalent attachment of PEDOT onto Pt and Pt/Ir electrodes using a two-step process, consisting of grafting of (4-thien-2-yl) diazonium salt onto the electrode using electrochemical reduction, followed by electropolymerization of PEDOT (Scheme 1). The electrode surface coverage is measured using the redox chemistry of ferrocene. The adhesion strength and stability of the PEDOT films with or without the grafted thienyl-derivative layer is evaluated using electrochemical cyclic voltammetry (CV) stress tests and ultrasonication.

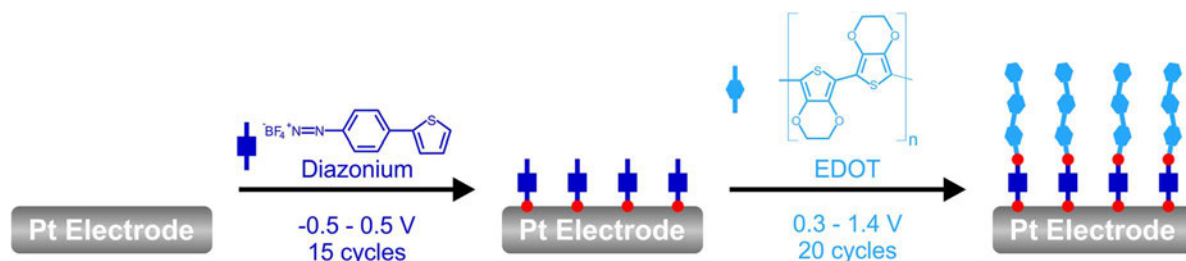
### Experimental

**Materials and reagents.**—All chemicals and solvents were ACS grade and used as received unless specified. 2-thiopheneboronic acid, 4-bromoaniline and tetrakis(triphenylphosphine) palladium (stored under Ar) were purchased from AK Scientific (Union City, USA). 3,4-ethylenedioxythiophene, tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) and sodium nitrite were purchased from Sigma-Aldrich (Oakville, Canada). Tetrafluoroboric acid (50%) were purchased from Alfa Aesar (Tewksbury, USA). Pt disk macroelectrodes were purchased from BASi (1.6 mm; Lafayette, USA) or CH Instruments (2 mm; Austin, USA). Pt/Ir microelectrodes were purchased from WPI Inc (PTM23B05; Sarasota, USA).

**Thienyl aniline and diazonium salt synthesis.**—(4-thien-2-yl)aniline was synthesized according to previously reported procedures (Scheme 2).<sup>31</sup> Briefly, 75 mL THF/Water (4:1 v/v) in a 250 mL three-neck flask was deoxygenized with argon for 1 h. Then, 4-iodoaniline (3.81 g, 17.4 mmol), thienylboronic acid (2.61 g, 20.4 mmol), sodium carbonate (19 g, 170 mmol) and tetrakis (triphenylphosphine) palladium (200 mg, 0.17 mmol) were added sequentially under argon. The reaction was stirred under reflux and argon for 16 h. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was dried with MgSO<sub>4</sub>. After removal of the solvent, a brown liquid was purified by flash chromatography, hexane/ethyl

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**Scheme 1.** Two-step process for covalent attachment of PEDOT on a Pt/Ir electrode. Grafting of the diazonium salt onto the Pt electrode surface, followed by polymerization of EDOT initiated on the thiophene moiety of the grafted layer.

acetate (8:1), producing an orange liquid, which was recrystallized in ethanol/water (1:1) to produce white crystals in a 61% yield.

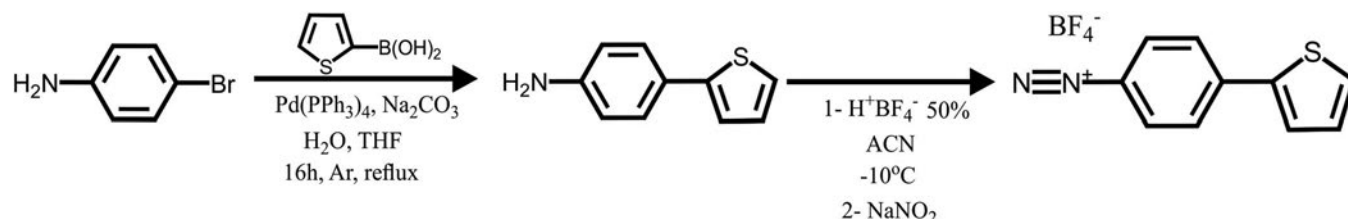
Diazotization of (4-thien-2-yl)aniline was performed according to previously reported procedures (Scheme 2).<sup>32</sup> Tetrafluoroboric acid 50% (124  $\mu$ L, 1 mmol) was added to (4-thien-2-yl) aniline (175 mg, 1 mmol) with dropwise addition of acetonitrile until dissolution. The solution was then cooled to  $-5^{\circ}\text{C}$ . An aqueous solution of saturated sodium nitrite (69 mg, 1 mmol) was added dropwise to the (4-thien-2-yl) aniline solution. The resulting suspension was filtered and was rinsed with cold ether.  $^1\text{H}$  NMR data for both products are included in the supporting information (Figures S1, S2).

**Electrochemical measurements and electropolymerization of PEDOT.**—Electrochemical measurements were performed using a Bio-Logic VMP3 multi-channel potentiostat. Potentials were recorded relative to a saturated Ag/AgCl reference electrode in a three-electrode setup using stainless steel mesh or Pt wire (0.5 mm) counter electrode.

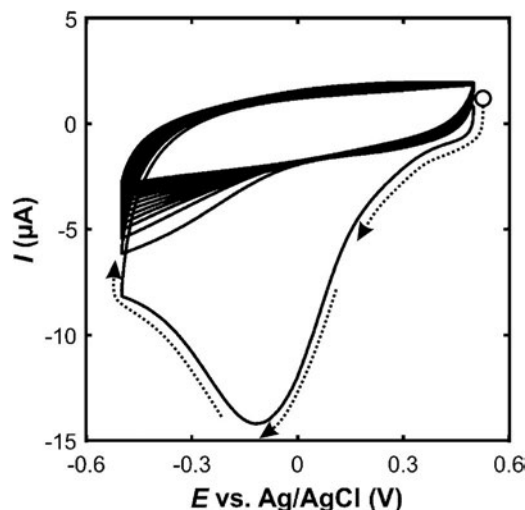
Pt disk macroelectrodes were manually polished using 0.05  $\mu\text{m}$  alumina on a microcloth (Buehler, Binghamton, USA) and rinsed with deionized water and acetonitrile. All solutions for cyclic voltammetry (CV) were prepared using 100 mM  $\text{LiClO}_4$  in acetonitrile with no degassing and all CV measurements were performed at a scan rate of  $0.1 \text{ V s}^{-1}$ . Diazonium reduction was performed using CV (15 cycles,  $-0.5$  to  $0.5 \text{ V}$ ,  $0.1 \text{ V s}^{-1}$ ) in a 5 mM solution of (4-thien-2-yl) diazonium salt. PEDOT electropolymerization was obtained from a 5 mM EDOT solution using CV (20 cycles,  $0.3$  to  $1.4 \text{ V}$ ,  $0.1 \text{ V s}^{-1}$ ). Surface coverage investigations were performed using a 5 mM ferrocene solution.

Pt/Ir microelectrodes were coated and characterized using the same parameters as for macroelectrodes, except for only 10 PEDOT polymerization cycles and the use of  $\text{TBABF}_4$  as an electrolyte instead of  $\text{LiClO}_4$ .

**Adhesion tests.**—The adhesion of PEDOT films was investigated using electrochemical stress tests and ultrasonication. For electrochemical stress tests, electrodes were immersed in phosphate-buffered saline (PBS, 0.1 M, pH 7.2) and subjected to 1000 stress cycles using CV ( $-0.6$  to  $0.6 \text{ V}$ ,  $0.1 \text{ V s}^{-1}$ ). In situ images of the electrode surface were acquired every 10 cycles using an inverted optical microscope (Electrochemical Probe Scanner 3, Heka Elektronik, Lambrecht, Germany). For ultrasonication, electrodes were immersed in deionized water for up to 10 min in a Branson 2510 Ultrasonic Cleaner (70 W). Images of the electrode surface were obtained using a customized Axio Vert.A1 inverted microscope (Zeiss, Oberkochen, Germany).



**Scheme 2.** Synthesis of (4-thien-2-yl) aniline and (4-thien-2-yl) aniline diazonium salt.

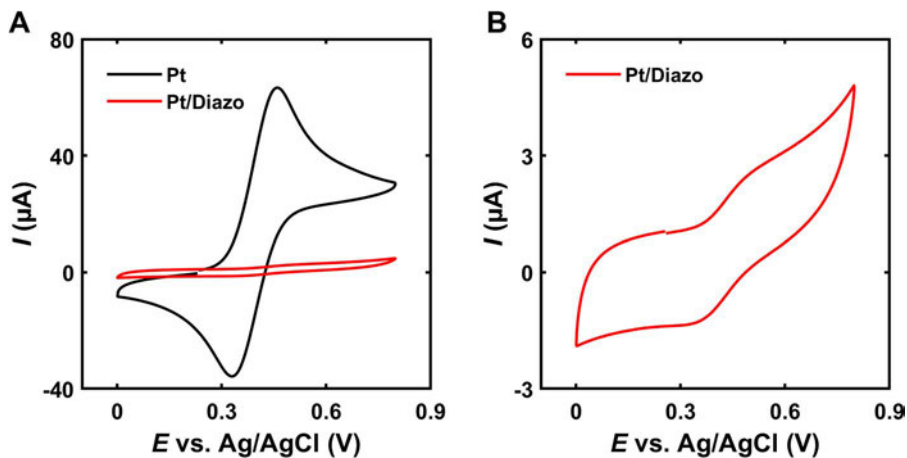


**Figure 1.** Electrochemical grafting of diazonium salt onto a Pt disk macroelectrode. CVs were performed in 5 mM (4-thien-2-yl) diazonium salt in 100 mM  $\text{LiClO}_4$  in acetonitrile (15 cycles,  $-0.5$  to  $0.5 \text{ V}$ ,  $0.1 \text{ V s}^{-1}$ ). Potentials are reported vs saturated Ag/AgCl. The dotted arrows outline the first cycle.

## Results and Discussion

**Diazonium grafting.**—The electrochemical grafting of diazonium salt on Pt disk macroelectrodes was performed using cyclic voltammetry (Figure 1). The voltammogram shows a broad irreversible reduction peak during the first cycle, centered at approximately  $-0.15 \text{ V}$  vs. Ag/AgCl. This irreversible peak corresponds to formation of a radical, which reacts with the electrode surface to form a covalent metal-carbon bond.<sup>25,28,29</sup> During subsequent cycles, this reduction peak is no longer observed, indicating the formation of a semi-permeable layer on the electrode surface i.e. the grafted diazonium salt forming a thin phenylthiophene film.

The surface coverage of the semi-permeable layer was further investigated using ferrocene (Fc), a redox mediator with well-defined reversible peaks. The electrochemical response of the disk macroelectrodes was measured before (Pt) and after (Pt/Diazo) diazonium grafting (Figure 2). The modified electrode (henceforth named Pt/Diazo)

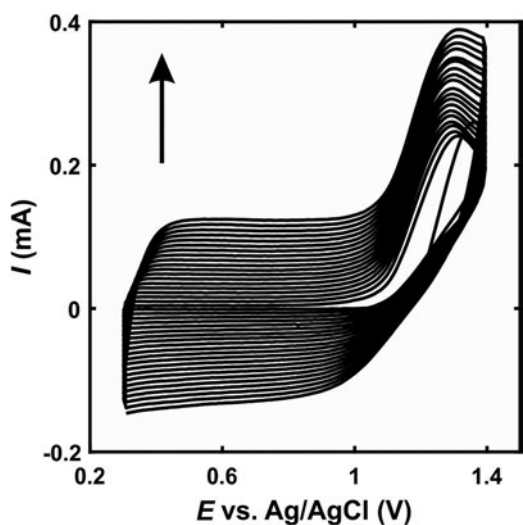


**Figure 2.** Characterization of the electrode surface after diazonium salt grafting. CVs were performed in 5 mM ferrocene in 100 mM LiClO<sub>4</sub> in acetonitrile (0 to 0.8 V, 0.1 V s<sup>-1</sup>). Potentials are reported vs saturated Ag/AgCl. A) Ferrocene redox chemistry on bare Pt (black) vs Pt/Diazo electrode (red). B) Magnification of the Pt/Diazo electrode response.

shows a substantial decrease of the redox current compared to the bare Pt, thereby confirming the presence of a film on the electrode surface (Figure 2A). Nevertheless, a small redox wave can still be detected on the magnified CV (Figure 2B), demonstrating that the grafted film is still slightly permeable to ferrocene molecules. The semi-permeable film allows for the oxidation of the thiophene moiety and initiation of the electropolymerization of PEDOT.

**Polymerization of PEDOT.**—After confirming the grafting of the diazonium layer, we carried out electropolymerization of PEDOT on the Pt/Diazo electrode. Despite the presence of the semi-permeable diazonium layer, the polymerization occurs readily and behaves similarly to PEDOT polymerization on a bare electrode surface (Figure 3). Using positive potentials, an irreversible oxidation peak appears at approximately 1.2 V, corresponding to the oxidation of the thiophene units covalently anchored to the electrode surface, followed by initiation of polymerization of the EDOT monomer in solution. Subsequent scans show an increase in current density for this peak, as the PEDOT film grows thicker and its electrochemical surface area increases.

**PEDOT adhesion.**—In order to evaluate the adhesion of the PEDOT films, Pt/PEDOT (i.e. physically adsorbed) and Pt/Diazo/PEDOT electrodes were subjected to two tests: electrochemical stress and ultrasonication.



**Figure 3.** Electropolymerization of PEDOT onto Pt/Diazo macroelectrode. CVs were performed in 5 mM EDOT in 100 mM LiClO<sub>4</sub> in acetonitrile (20 cycles, 0.3 to 1.4 V, 0.1 V s<sup>-1</sup>). Potentials are reported vs saturated Ag/AgCl. The arrow indicates the increase in current of subsequent cycles.

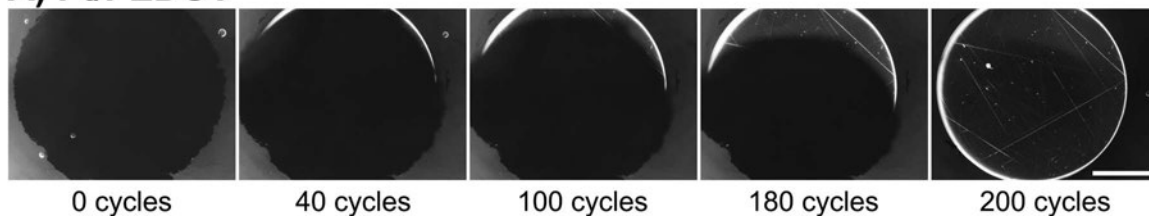
During repeated oxidation/reduction cycles, conducting polymers maintain charge neutrality by uptake or release of ions and solvent, resulting in substantial volume change and thus physical stress.<sup>33</sup> Pt/PEDOT and Pt/Diazo/PEDOT electrodes were subjected to extensive voltammetric cycling in PBS. This electrochemical stress test is an accelerated analogue to the working environment of implanted neural electrodes. The adhesion of the PEDOT film on each electrode was measured in situ using an inverted optical microscope (Figure 4). The physically adsorbed PEDOT films (Pt/PEDOT) begin to delaminate after 40 cycles, and all tested electrodes were completely delaminated before 200 cycles ( $n = 5$ ). Unlike the work of Boehler and coworkers,<sup>22</sup> there was no apparent damage to the films before delamination, which may be due to the use of a different counter ion for polymerization i.e. PSS vs perchlorate. In the case of covalently attached films (Pt/Diazo/PEDOT), all seven tested electrodes maintained their initial morphology beyond 1000 cycles. This comparison clearly demonstrates the improved adhesion properties resulting from the covalent attachment of the PEDOT films on the Pt electrode.

Beyond their morphology, Pt/Diazo/PEDOT electrodes also maintained their electrochemical performance, showing only a 20% decrease in current density after 1000 cycles (Figure 5).

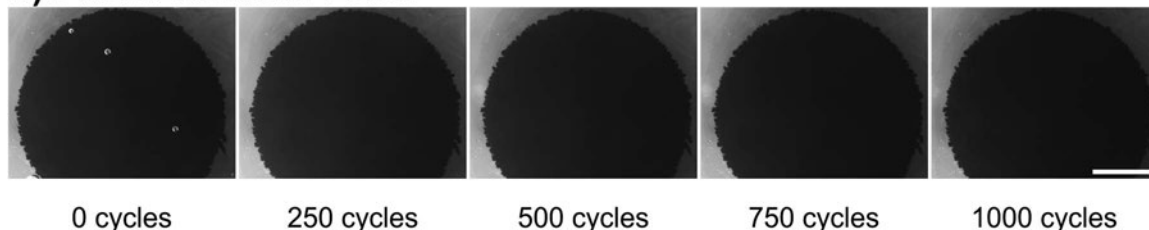
In addition to the improved adhesion on metal, demonstrated by electrochemical stress testing, conducting polymer coatings for implanted neural electrodes need to show long lifetime. Therefore, Pt/PEDOT and Pt/Diazo/PEDOT electrodes were subjected to ultrasonication, i.e. a much harsher aging test, to determine their long-term viability (Figures 6A–6B). As expected, physically adsorbed films (Pt/PEDOT) completely delaminated after 10 s (Figure 6A). However, (Pt/Diazo/PEDOT) withstood ultrasonication for more than 10 min with no apparent damage (Figure 6B). Furthermore, similar to the results of the electrochemical stress testing, Pt/Diazo/PEDOT electrodes maintained their electrochemical performance after 15 min of ultrasonication (Figure 6C). Considering that they could survive this extremely harsh environment, covalently attached PEDOT films are mechanically and electrochemically viable for long-term implantation.

**Application to neural microelectrodes.**—Having confirmed the substantially improved adhesion and stability of covalently attached PEDOT films on Pt disk macroelectrodes, the two-step process was applied to the fabrication of microelectrodes destined for brain implantation. These commercially available conical microelectrodes consisted of a Pt/Ir core surrounded by a parylene insulating layer. Despite large differences in electrode geometry (disk vs. conical), dimensions (2 mm vs. 1–2  $\mu\text{m}$  diameter), and composition (Pt vs. Pt/Ir), the covalent attachment of PEDOT using an intermediate diazonium layer was also successful on these microelectrodes (Figure 7). Similar to the results on the large Pt macroelectrode, covalently attached PEDOT withstood aggressive sonication, unlike physically adsorbed PEDOT. It should be noted that during electropolymerization, the growth of

## A) Pt/PEDOT



## B) Pt/Diazonium/PEDOT

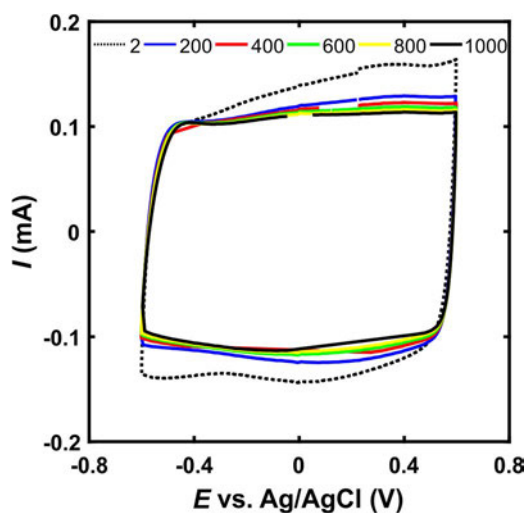


**Figure 4.** Optical micrographs of PEDOT film during electrochemical stress test. A) Pt/PEDOT B) Pt/Diazonium/PEDOT. Scale bars represent 0.5 mm. CVs were performed in PBS solution (1000 cycles,  $-0.6$  to  $0.6$  V,  $0.1$  V  $s^{-1}$ ). Potentials are reported vs saturated Ag/AgCl.

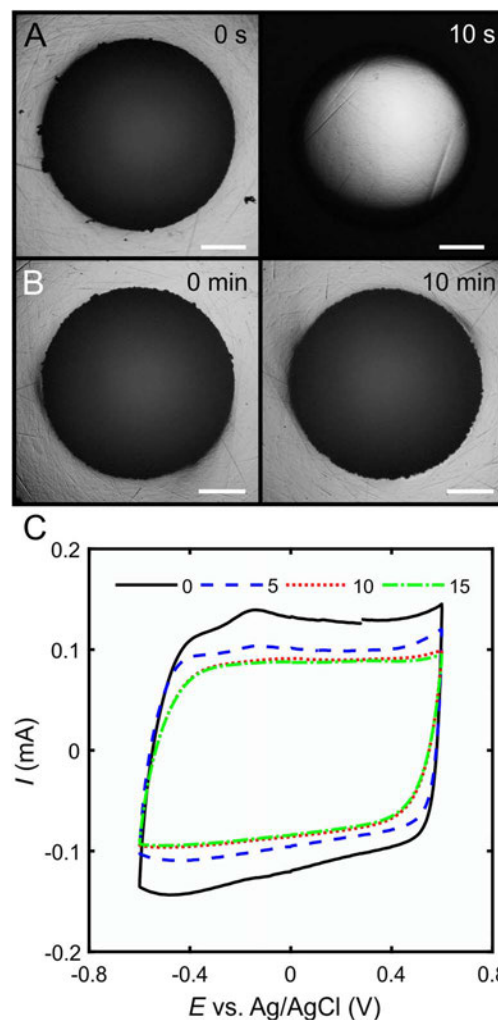
the PEDOT layer seems to extend beyond the Pt/Ir tip, over the parylene insulating layer. This may be due to the use of organic solvent for diazonium salt grafting and electropolymerization, which could cause a swelling of the thin insulating parylene layer, resulting in a relatively poor insulation. Nevertheless, after only 1 min of sonication, the physically-adsorbed PEDOT film completely delaminated from the Pt/Ir tip (Figure 7, bottom left panel), while the covalently attached PEDOT remained on the microelectrode tip after more than 10 minutes of sonication, although part of the deposited polymer was removed. Consequently, the proposed diazonium attachment strategy was successful at both the macro and microscale. Equivalent electrochemistry data for microelectrodes is included in supporting information (Figures S3-S5).

## Conclusions

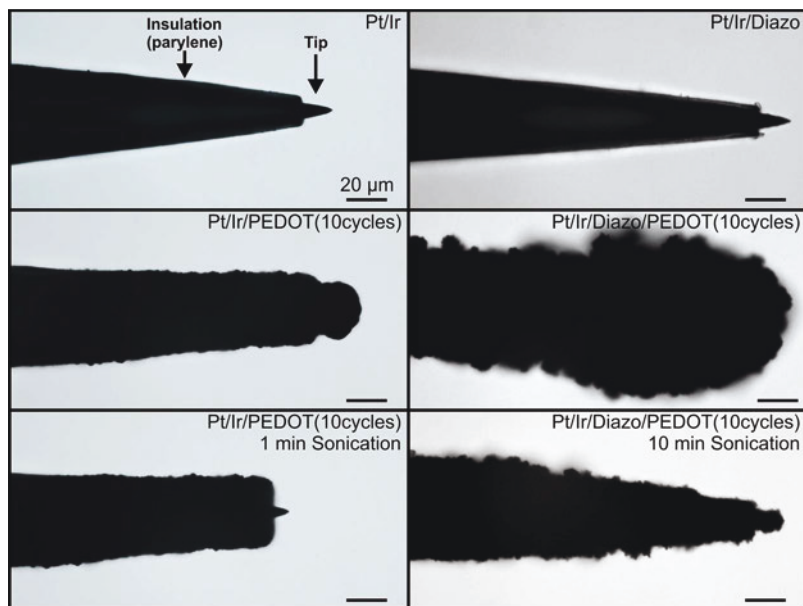
We have shown that a PEDOT film can be covalently attached to a Pt or Pt/Ir electrode surface by depositing an intermediate layer of phenylthiophene using diazonium salt reduction. Covalently attached



**Figure 5.** Electrochemical performance of Pt/Diazo/PEDOT electrode during electrochemical stress test (cycle 2, 200, 400, 600, 800, and 1000). CVs were performed in PBS solution ( $-0.6$  to  $0.6$  V,  $0.1$  V  $s^{-1}$ ) Potentials are reported vs saturated Ag/AgCl.



**Figure 6.** Effect of ultrasonication on PEDOT films. Optical micrographs of PEDOT coating after ultrasonication. A) Pt/PEDOT and B) Pt/Diazo/PEDOT. C) Electrochemical performance of Pt/Diazo/PEDOT electrode before (0 min) and after sonication (5, 10, 15 min). CVs were performed in PBS solution ( $-0.6$  to  $0.6$  V,  $0.1$  V  $s^{-1}$ ). Scale bars represent 0.5 mm. Potentials are reported vs saturated Ag/AgCl.



**Figure 7.** Optical micrographs of neural microelectrodes before polymerization, after polymerization, and after sonication. The left panel shows a Pt/Ir/PEDOT microelectrode, while the right panel shows a Pt/Ir/Diazo/PEDOT microelectrode. Scale bars represent 20  $\mu\text{m}$ .

PEDOT showed superior adhesion properties compared to physically adsorbed PEDOT, withstanding over 1000 cycles of CV and 10 min of ultrasonication without losing any significant electrochemical performance. This new electrode architecture will be particularly useful for applications requiring long-term stability, such as DBS. This simple two-step attachment strategy can be readily adapted to different surface functionalization of Pt and Pt/Ir, given the wide variety of diazonium salts already available.

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