

Short Communication

## A Facile Fabrication of Microelectrodes with Recyclable Feature using Organic Soluble Wax

Qinghua Liu<sup>1,2,\*</sup>, Wenyuan Yan<sup>1</sup>, Yanan Li<sup>1</sup>, Feimeng Zhou<sup>1</sup>

<sup>1</sup> College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, P.R. China

<sup>2</sup> School of Chemistry and Chemical Engineering, Heze University, Heze 274015, China

\*E-mail: [liuqinghua-126@126.com](mailto:liuqinghua-126@126.com)

Received: 4 January 2020 / Accepted: 18 February 2020 / Published: 10 April 2020

Here, a facile, low-cost and recyclable method for the fabrication of electrodes. Organic soluble wax sealing allows one to bypass the complicated laser-pulling and torch-sealing used in conventional fabrication protocols. Electrodes with various electrode wires were successfully fabricated, including platinum (e.g., 200, 100, 76, and 25  $\mu\text{m}$ ) and carbon fiber (11  $\mu\text{m}$ ). Our electrodes are feasible and convenient to recycle due to the good solubility of wax in acetone. The fabricated electrodes are then characterized by cyclic voltammetry in  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$  and dopamine solutions. The CV curves show well-defined peak and sigmoidal responses, which confirms the successful fabrication of ideal conventional-sized electrodes and microelectrodes.

**Keywords:** Organic soluble wax; Microelectrodes; Recyclable; Carbon fiber; Cyclic voltammetry

### 1. INTRODUCTION

Electrodes are generally divided into two categories: traditional-sized electrodes (e.g., disc electrodes with diameters greater than 25  $\mu\text{m}$ ) and microelectrodes [1]. The use of the microelectrodes extends electrochemically conventional methods to more complicated conditions [2, 3]. Compared with traditional-sized electrodes, the application of microelectrodes can reduce sample volume, improve sensitivity, enhance mass transport, and decrease ohmic loss and double-layer capacitance, leading to a higher signal-to-noise ratio [1, 4-6]. This is due to the fact that the Faraday current increases with decrease of the area of the working electrode, and the residual current are also proportional to the area of the working electrode under convergent diffusion [7].

Over the past decades, the technologies for fabrication of electrodes have been largely improved. Glasses with epoxy [8] or Teflon [9] are the most commonly used materials in fabrication of the conventional-sized electrodes. However, the sealing is difficult and inappropriate due to the conflict

between hydrophobic polymers and hydrophilic metals. In addition, if the electrode is not sealed well, it would be easily damaged or even cause to leak, which will increase the cost because these electrodes are expensive and unrecyclable. Compared with the fabrication of the conventional-sized electrodes, the microelectrodes fabrication is more difficult, time-consuming and expertise-demanding. Therefore, it is necessary to set up a facile method for fabricating electrodes with recyclable character.

There are two conventional techniques for manufacturing microelectrodes, one is to seal metal wires in glass filaments by heating, and the other is a laser-based micropipette drawing system [10, 11]. The former generally uses a torch to close one end of the glass capillary, and then seals the metal wire with a heated coil. The latter requires a laser-based micropipette puller system to seal and pull the glass capillary with an inside metal wire. However, because the thermal expansion coefficient of metal wires cannot match with that of the glass capillary, bubbles are easily generated during cooling process. The bubbles will increase the resistance and decrease the experimental sensitivity and accuracy [12]. Besides, glass-insulated electrodes cannot be used in concentrated alkaline solution. To solve this problem, several methods are developed and applied to the fabrication of microelectrodes, especially for the carbon fiber microelectrodes. In recent decades, carbon fiber microelectrodes are widely used in biological species such as extracellular fluid and neurotransmitters [2, 13]. In addition to the above encapsulation method, a number of alternative routes have been developed to prepare the carbon fiber microelectrodes, including pyrolysis [14], argon ion beam etching [15], and 3D-printed [16]. Noteworthily, these methods are only suitable for cutting-edge science, as the large cost of time and money renders it nonideal in basic application.

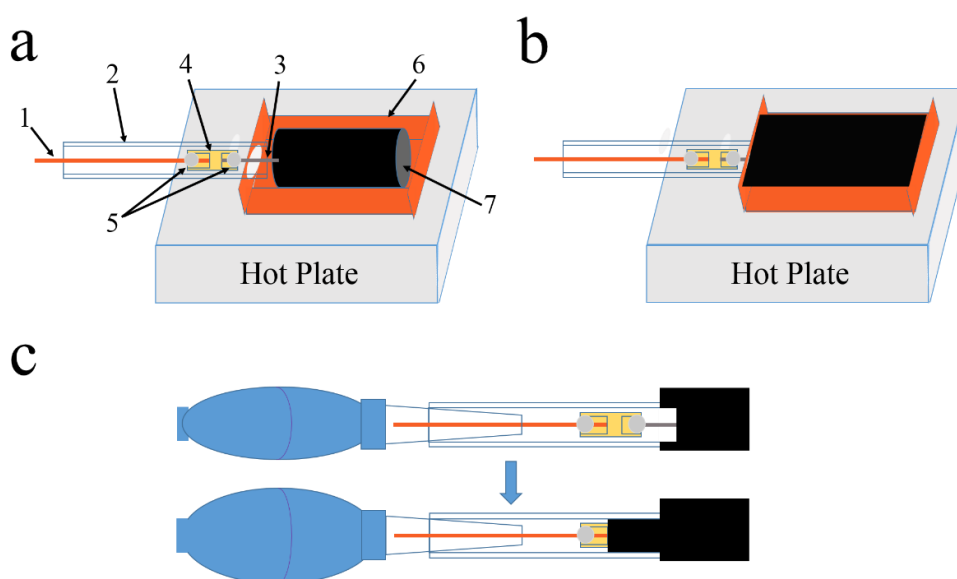
Apiezon wax is a cheap material which was used to seal scanning tunneling microscope (STM) tips [17] and has not been used in conventional-sized electrode preparation, and more important, the electrodes sealed by organic soluble wax, unlike those sealed by other polymer encapsulating materials which will leak when it was cracked even if it is only damaged on the surface, and cannot be reused, can be recycled after polishing the damaged part as the wax can be dissolved in acetone. In this paper, we present a facile, low-cost and recyclable method which can be used to prepare both conventional-sized electrodes and microelectrodes with different electrode materials, such as platinum and carbon fiber. It elaborates a simple encapsulation method: insulating the electrode with molten organic soluble wax under negative pressure provided by a cheap rubber suction bulb. This encapsulation method can be used to prepare conventional-sized electrodes and microelectrodes of high quality, especially carbon fiber microelectrodes in this paper.

## 2. EXPERIMENTAL SECTION

### 2.1. Chemicals and materials.

Electrode fabrication materials used were Platinum wire (purity 99.99+%, 200, 100, 76, and 25  $\mu\text{m}$  in diameter, Sigma-Aldrich, St. Louis, USA), and carbon fiber (11  $\mu\text{m}$  diameter, Amoco Thornel P-55S, 4K, Chicago, IL, USA). Borosilicate capillaries (outer diameter: 3.1 mm, inner diameter: 1.8 mm) were received from Sutter Instruments (Novato, CA, USA). Electrically conductive silver epoxy was

purchased from Epoxy Technology Inc. (EPO-TEK H2OE, Billerica, MA, USA). Sealing material was Apiezon wax W acquired from Apiezon (approximate softening point: 80 to 90 °C, Manchester, UK), which can offer efficient joint sealing over wide temperature range and the resistance to attack by acids and alkalis. Polishing materials were received from Buehler (Lake Bluff, IL, USA), including abrasive discs (400, 800, 1200 grit), nylon cloth, diamond polishing compound (15, 6, and 1  $\mu\text{m}$ ), microcloth and alumina suspensions (0.3, 0.1, 0.05  $\mu\text{m}$  particle diameter). KCl, NaCl,  $\text{Na}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$  (purity 99%, Guoyao Co. Ltd., Shanghai, China) were used to prepared the phosphate buffer solution (135 mM NaCl, 2.7 mM KCl, 8 mM  $\text{Na}_2\text{HPO}_4$  and 1.5 mM  $\text{KH}_2\text{PO}_4$ , PH 7.2). Potassium Ferricyanide (purity 99%, Sigma-Aldrich, St. Louis, MO, USA) and dopamine hydrochloride (purity 98%, Alfa Aesar, Ward Hill, MA, USA) were used as received for the electrochemical measurement. Aqueous solutions were prepared with deionized water (18.2  $\text{M}\Omega/\text{cm}$ ; Simplicity 185, Millipore Corp, Billerica, MA, USA). All solutions were purged with nitrogen for 20 min prior to cyclic voltammetry.



**Figure 1.** Schematic representation of the electrode preparation. (1) copper wire, (2) glass tube, (3) electrode wires, (4) copper connector, (5) silver epoxy, (6) copper foil box and (7) organic soluble wax for manipulator. (a) Connecting the electrode wire with copper wire by copper connector and silver epoxy, and inserting into the hole of the copper foil box; (b) Heating the wax on the hotplate; (c) Sealing the electrode with hot wax and rubber suction bulb.

## 2.2 Fabrication of electrode

A complete schematic of the electrode fabrication technique is presented in Figure 1. The electrode wires (platinum wires and carbon fiber) and borosilicate capillaries were initially cleaned in an ultrasonic bath successively in acetone, ethanol and nanopure water. One end of an electrode wire was connected to a 0.5 mm copper wire with silver epoxy and a copper connector, which was subsequently baked for 20 min at 120 °C. The assembly was then inserted into a borosilicate capillary which provides protection and insulation. The unsealed electrode needs to horizontally insert into the

matched hole on one side of a copper foil box before heating to avoid wax leakage (Figure 1a). The copper foil box was heated on the hotplate to evenly melt the organic soluble wax (Figure 1b). The melted wax was then slowly inhaled into the capillary with the aid of rubber suction bulb and the copper connector must be covered by wax, in order to ensure that the electrode wire is fixed on the inner wall of the capillary by wax (Figure 1c). The surrounded wax could be easily wiped off and the transparent glass tube is beneficial to assess the quality of the electrodes. In addition, a part of the electrode wire was always exposed outside the borosilicate capillary allowing us to conveniently identify the electrode. The exposure is important to fabricate the carbon fiber microelectrodes, due to the small diameter and similar color to the wax and easy break when the wax was inhaled into the borosilicate capillary. The exposed electrode wires and wax were cut down followed by a final polishing step, using diamond polishing compound and alumina suspensions. However, excess exposure of electrode wire is unnecessary and wasteful when the electrode surface can be easily found by the naked eye or with an optical microscope after simply polishing. The fabrication procedure is simple to yield consistently high-quality electrodes without any prior electrode fabrication experience. Total time for a single electrode fabrication was less than 1h and several electrodes could be produced in sequence, making it possible for volume production.

We also recycled the as-prepared electrodes. At first, the electrode was heated on a hotplate (100 °C) to soften the wax. Then, the electrode wire was pulled out of the borosilicate capillary from the copper wires end and immersed in acetone and ultrasonically cleaned. After rinsed by acetone for three times and dried in air, the metal wires were recycled. The subsequent fabrication process of electrode was the same as above procedures.

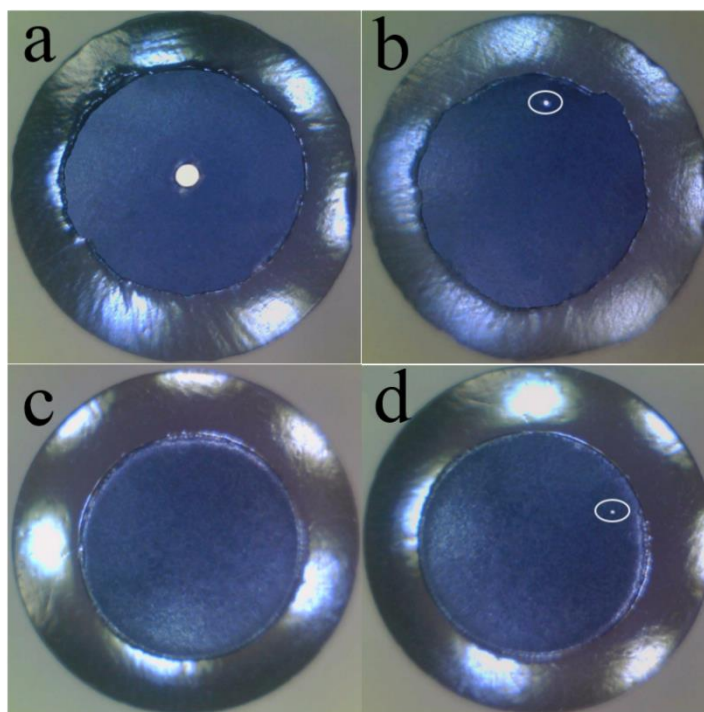
### 2.3. Characterization

Optical micrographs were obtained by a metallurgical microscope (NJF-120A, Novel optics, Ningbo, China). Electrochemical performance was characterized by cyclic voltammetry curves, which were performed by a CHI 760e electrochemical workstation (CHI instrument, Shanghai, China) in a three-electrode setup with Ag/AgCl and platinum wire as reference and counter electrode, respectively. Potassium ferricyanide was used for Au, Pt, and carbon fiber electrode measurements and potassium chloride was used as a supporting electrolyte. The Pt and carbon fiber electrodes were used to detect dopamine in a phosphate buffer solution. For cyclic voltammetry using Potassium ferricyanide, the potential was varied linearly from 0.5 to  $-0.1$  V vs. Ag/AgCl, while a window of 0 to 0.4 V vs. Ag/AgCl was used with dopamine. The cyclic voltammograms were performed using different scan rates. All experiments were performed in a Faraday cage.

## 3. RESULTS AND DISCUSSION

Figure 2(a-b) and (c-d) show top views of platinum and carbon fiber electrodes, respectively. Due to the small diameter and similar surface as the organic soluble wax, carbon fiber is difficult to be

observed directly (Figure 2c). However, it became visible after electroplating gold (Figure 2d). The optical micrographs indicate both the platinum electrode and carbon fiber electrode possess ideal disk geometry. It also proves that this developed method can be used for fabricating both conventional-sized electrodes and microelectrodes. The smooth surface and absence of pits or holes indicate that electrodes wires have been tightly sealed into the borosilicate capillary by the organic soluble wax, diminishing the undesirable contact. This inexpensive encapsulating material can also avoid the bubble presence due to the difference in thermal expansion coefficient between the electrode wire (Pt,  $9 \times 10^{-6} / \text{K}$ ; Au,  $14.2 \times 10^{-6} / \text{K}$ ) [18] and borosilicate capillary ( $3.3 \times 10^{-6} / \text{K}$ ) [19]. Owing to the lower melting point of the organic soluble wax, its plasticity can compensate for the deformation of electrode wires and borosilicate capillary during heating. Both traditional techniques for making microelectrodes have problems with air bubbles. The technology of directly sealing a metal wire in a glass filament by heating makes it easy to generate air bubbles during cooling due to the difference in thermal expansion coefficient [10, 20]. Laser-based micropipette stretching systems require complex vacuum systems to minimize bubble generation [11, 21].



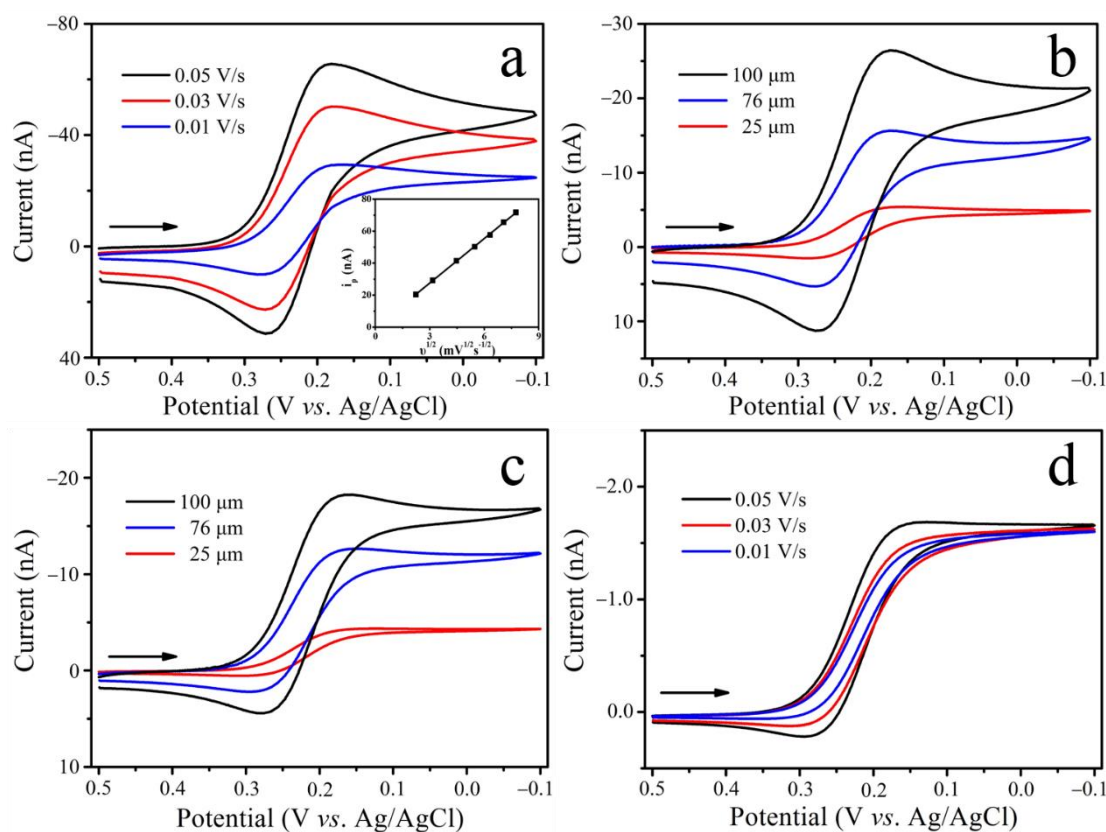
**Figure 2.** Top view optical micrographs for platinum electrodes of (a) 200  $\mu\text{m}$ , (b) 25  $\mu\text{m}$  and carbon fiber (11  $\mu\text{m}$ ) before (c) and after (d) electroplating gold, using reflected light.

To characterize the electrochemical behavior of electrodes in different sizes, cyclic voltammetry was performed. When linear diffusion exists on the surface of conventional-sized electrode, the current always possesses a peak value even at a small scan rate, because of the limitation of the mass transfer [22]. If the characteristic redox time is small enough to allow the diffusion film to be considered as a

classical semi-infinite diffusion field, the classical diffusion equation for cyclic voltammetry should be approximately applicable. The characteristic of the reversible charge transfer reaction is in dependence of the peak height on the square root of the scan rate. At 25 °C the peak current is given by

$$i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} \nu^{1/2} C_0^* \quad (1)$$

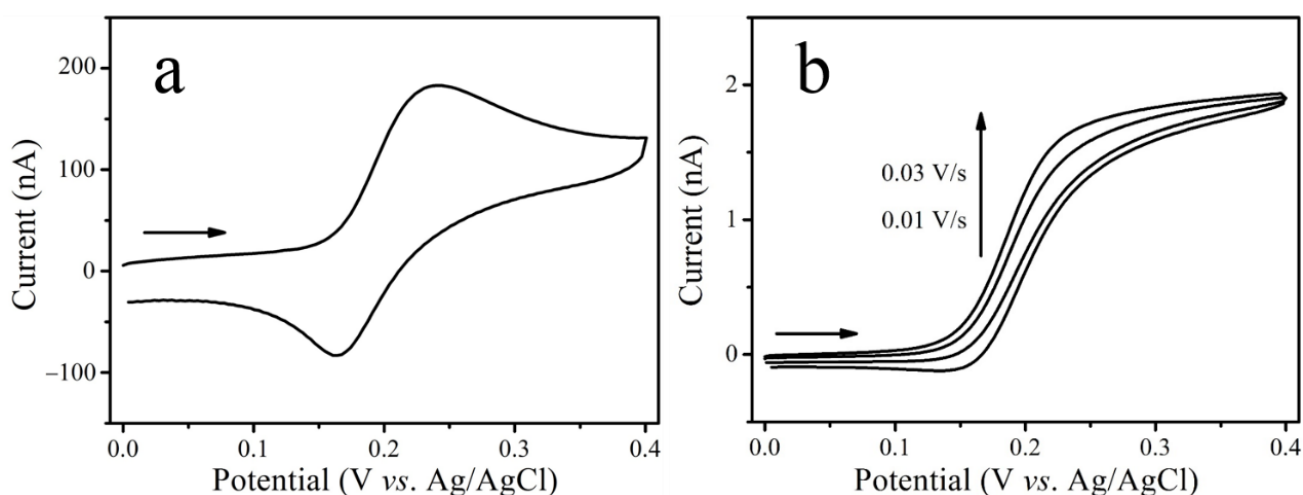
where  $i_p$  is the peak current (A),  $n$  the number of electrons involved in the charge transfer reaction,  $D_0$  the diffusion coefficient of the species responsible for the charge transfer ( $\text{cm}^2/\text{s}$ ),  $\nu$  the sweep rate (V/s) and  $C_0^*$  the bulk concentration (moles/ $\text{cm}^3$ ). Figure 3a shows a typical peak-shaped voltammograms at 200  $\mu\text{m}$  Pt electrode in 1 mM  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$ . The separation in the peak potentials close to 59/n mV indicates the redox reaction is reversible and the diffusion coefficients for the oxidized and reduced forms are the same [23]. The cathodal peak currents  $i_p$  increased with the increase of the sweep rate, exhibiting a linear relationship to the square root of the scan rate and pass through the origin (insert of Figure 3a). It indicates that the electron transfer reaction on large-sized electrode is controlled by the diffusion of redox species, yielding semi-infinite linear diffusion [24].



**Figure 3.** (a) Cyclic voltammograms of 1 mM  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$  in 0.1 M KCl at 200  $\mu\text{m}$  Pt electrode. Inset: Plot of the peak currents versus square root of the scan rates. Cyclic voltammograms of 1 mM  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$  in 0.1 M KCl at the scan rate of 0.05 V/s (b) and 0.01 V/s (c), at Pt electrodes of 100  $\mu\text{m}$  (black), 76  $\mu\text{m}$  (blue) and 25  $\mu\text{m}$  (red). (d) Cyclic voltammograms of 1 mM  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$  in 0.1 M KCl at carbon fiber microelectrode.

The rate of diffusion plays an important role in defining the shape of voltammograms. Different from the peak-shaped curves generated by diffusion control on conventional-sized electrodes, the voltammograms are analogous to the S-shaped polarograms obtained at the microelectrodes, because of

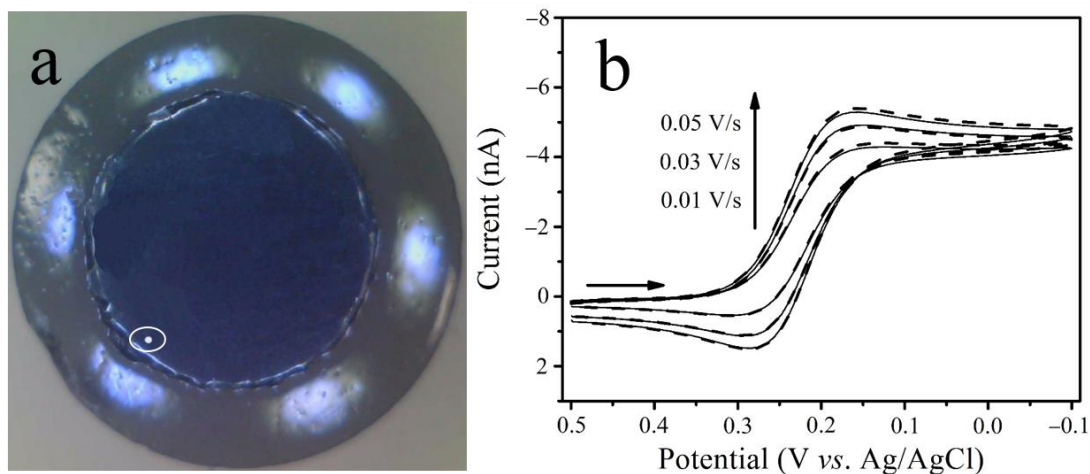
the change from essentially linear diffusion at short times to spherical diffusion at long times [25]. Figure 3(b) and 3(c) show the cyclic voltammograms of  $K_3[Fe(NH_3)_6]$  at the intermediate-sized electrodes (100, 76 and 25  $\mu m$ ). Although the peak current decreases as the electrode size decreases, the shape of the curve gradually changes from a peak-shaped to an S-shaped (Figure 3b). In addition, the reaction at low scan rate is less affected by the diffusion rate than that at high scan rate. Compared with the curves in Figure 3b, the CV curves (Figure 3c) at lower scan rate resembles more as S-shaped, exhibiting more characteristics of steady-state currents. A typical S-shaped CV curve were shown in Figure 3d at carbon fiber microelectrode and the responses on the forward and reverse scans were almost the same. It indicates that ideal carbon fiber microelectrodes were also fabricated by this method with varying sizes of metal electrodes [25].



**Figure 4.** Cyclic voltammograms of 1 mM dopamine in 0.01 M phosphate buffer solution (a) at 200  $\mu m$  Pt electrode (0.1 V/s) and (b) carbon fiber microelectrode.

Dopamine is a neurotransmitter that is released at the synaptic cleft between two neurons. The neurotransmission is related to various behaviors including reward mechanisms in the brain and motivational habit [26]. Electrochemical measurements are ideally suitable for detection of several physiological parameters of dopamine. The electrochemical oxidation of dopamine involves two electrons and two protons, which occurs at around 0.2 V vs. Ag/AgCl [27]. Figure 4 shows the cyclic voltammograms obtained from dopamine at prepared conventional-sized electrode (a) and microelectrode (b). The pair of typical redox peaks of dopamine demonstrates that the electron transport at the conventional-sized electrode is still limited by the rate of adsorption/desorption on the electrode surface, due to the mass transport (Figure 4a). Many studies have been done on monitoring the dopamine in vivo using carbon fiber microelectrodes with voltammetric measurements [2, 13, 14, 28]. Figure 4b shows the well-defined cyclic voltammograms of dopamine at prepared carbon fiber microelectrode in this paper. Typical steady-state responses were observed at slow scan rates with minimal background charging current, indicating the carbon fiber microelectrodes produced via this simple method have superior performance and can be applied to cutting-edge fields such as biochemistry and neuroscience.

Since the electrochemical methodology was introduced to broad new domains of space, it extended the application fields of electrodes and chemical medium [29]. Complex detection environment brings more risk to contaminate or damage the electrodes, especially in alkaline condition [30]. Polishing only solves the surface problem and additional microelectrode will increase the cost. Hence, reproducibility is an important feature for the preparation method in this paper, especially for the noble metals electrodes.



**Figure 5.** (a) Top view optical micrograph for recycled 25  $\mu\text{m}$  Pt electrode. (b) Cyclic voltammograms of 1 mM  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$  in 0.1 M KCl at prepared 25  $\mu\text{m}$  Pt electrode (solid lines) and recycled 25  $\mu\text{m}$  Pt electrode (dash lines).

Figure 5 (a) show the top view optical micrograph of the 25  $\mu\text{m}$  Pt electrodes after recycled. Compared to the electrode before recycled (Figure 2b), both of them conform smooth microelectrodes surrounded by insulating sheath. The tightly filling ensures the absence of undesired contact between the metal wire and solution. The corresponding CVs in  $\text{K}_3[\text{Fe}(\text{NH}_3)_6]$  solutions were exhibited in Figure 5(b) at different scan rates. The near curves under the same condition indicate the feasibility of recycle and the negligible capacitive current also demonstrate the well insulation and sealing. Therefore, even if an electrode is damaged, using this method, the electrode wire can be reused to prepare a new electrode with almost the same performance as the original electrode, avoiding the inconsistent results obtained at other electrodes. In addition, the recycled electrode wire can also be sealed with different material tubes, which is convenient for different reaction conditions.

#### 4. CONCLUSIONS

The electrodes are readily constructed by sealing the electrode wires into the borosilicate capillary with organic soluble wax, which is cheap and facile. This method is also versatile since it is suitable for both conventional-sized electrodes and microelectrodes. Since the wax can be easily dissolved in acetone, recyclability is also an advantage of this fabrication method. A key processing parameter here is the heating temperature and exposing excess electrode wire is also important to fabricate carbon fiber microelectrodes. The procedure employed can be further extrapolated to other



kinds of electrodes, such as ring, micro-disc array and microband. The method described may find utility in electrochemical probe fabrication as well.

#### ACKNOWLEDGMENTS

This work received financial support from a 2011 Collaborative Innovative Grant of Hunan Province of China.

#### NOTES

The authors declare no competing financial interest.

#### References

1. A. M. Bond, *Analyst*, 119 (1994) 1R.
2. R.M. Wightman, *Science*, 311 (2006) 1570.
3. I. Montenegro, M.A. Queirós, J.L. Daschbach, *Microelectrodes: Theory and Applications*, Kluwer, (1991) Dordrecht, The Netherlands.
4. D. Di, H. Wang, X. Wu, P. Dong, C. Wang, J. Wang, J. Chen, S. Li, *Int. J. Electrochem. Sci.*, 9 (2014) 3618.
5. C. Yang, C.B. Jacobs, M.D. Nguyen, M. Ganesana, A.G. Zestos, I.N. Ivanov, A.A. Puretzky, C.M. Rouleau, D.B. Geohegan, B.J. Venton, *Anal. Chem.*, 88 (2016) 645.
6. K. Wang, C.L. Frewin, D. Esrafilzadeh, C. Yu, C. Wang, J.J. Pancrazio, M. Romero-Ortega, R. Jalili, G. Wallace, *Adv. Mater.*, 31 (2018) 1805867.
7. K.R. Wehmeyer, M.R. Deakin, R.M. Wightman, *Anal. Chem.*, 57 (1985) 1913.
8. C. Lee, C. J. Miller, A. J. Bard, *Anal. Chem.*, 63 (1991) 78.
9. J. Rodriguez-Lopez, M.A. Alpuche-Aviles, A.J. Bard, *Anal. Chem.*, 80 (2008) 1813.
10. B. Zhang, K.L. Adams, S.J. Lubner, D.J. Eves, M.L. Heien, A.G. Ewing, *Anal. Chem.*, 80 (2008) 1394.
11. M.A. Mezour, M. Morin, J. Mauzeroll, *Anal. Chem.*, 83 (2011) 2378.
12. A.M. Bond, D. Luscombe, K.B. Oldham, C.G. Zoski, *J. Electroanal. Chem.*, 249 (1988) 1.
13. L. Zhou, H. Hou, H. Wei, L. Yao, L. Sun, P. Yu, B. Su, L. Mao, *Anal. Chem.*, 91 (2019) 3645.
14. E. Peltola, J.J. Heikkinen, K. Sovanto, S. Sainio, A. Aarva, S. Franssila, V. Jokinen, T. Laurila, *J. Mater. Chem. B*, 5 (2017) 9033.
15. B.X.E. Desbiolles, E.D. Coulon, A. Bertsch, S. Rohr, P. Renaud, *Nano Lett.*, 19 (2019) 6173.
16. E. Trikantopoulos, C. Yang, M. Ganesana, Y. Wang, B.J. Venton, *Analyst*, 141 (2016) 5256.
17. L.A. Nagahara, T. Thundat, S.M. Lindsay, *Rev. Sci. Instrum.*, 60 (1989) 3128.
18. D.E. Gray, American Institute of Physics Handbook (3rd ed), (1972) New York, USA.
19. M.M. Lima, R. Monteiro, *Thermochim. Acta*, 373 (2001) 69.
20. U.K. Sur, A. Dhason, V. Lakshminarayanan, *J. Chem. Educ.*, 89 (2012) 168.
21. L. Danis, D. Polcari, A. Kwan, S.M. Gateman, J. Mauzeroll, *Anal. Chem.*, 87 (2015) 2565.
22. M. Seo, J.H. Bae, D.W. Hwang, B. Kwak, J. Yun, S.Y. Lim, T.D. Chung, *Electrochim. Acta*, 258 (2017) 90.
23. X. Zheng, X. Zhou, X. Ji, R. Lin, W. Lin, *Sensor. Actuat. B-Chem.*, 178 (2013) 359.
24. S. Fryars, E. Limanton, F. Gauffre, L. Paquin, C. Lagrost, P. Hapiot, *J. Electroanal. Chem.*, 819 (2018) 214.
25. H. Tatsumi, S. Tanaka, *Electrochim. Acta*, 135 (2014) 255.
26. I.M. Taylor, N.A. Patel, N.C. Freedman, E. Castagnola, X.T. Cui, *Anal. Chem.*, 91 (2019) 12917.
27. C.R. Raj, T. Okajima, T. Ohsaka, *J. Electroanal. Chem.*, 543 (2003) 127.
28. W.-H. Huang, D.-W. Pang, H. Tong, Z.-L. Wang, J.-K. Cheng, *Anal. Chem.*, 73 (2001) 1048.

29. C.G. Zoski, *Electroanal.*, 14 (2015) 1041.

30. J. Cvačka, V. Quaiserová, J. Park, Y. Show, A. Muck, G.M. Swain, *Anal. Chem.*, 75 (2003) 2678.

© 2020 The Authors. Published by ESG ([www.electrochemsci.org](http://www.electrochemsci.org)). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).