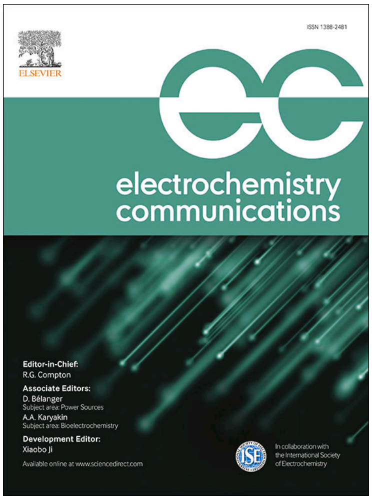

Preparation and electrochemical performance of TEMPO-modified polyterthiophene electrode obtained by electropolymerization

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Preparation and electrochemical performance of TEMPO-modified polyterthiophene electrode obtained by electropolymerization

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Graphical abstract

Highlights

A novel terthiophene monomer with a side chain TEMPO (TT-TEMPO) was synthesized successfully.

The polymer PTT-TEMPO film displayed a uniform network structure.

The PTT-TEMPO film electrode functioned well for selective oxidation of benzyl alcohol to benzaldehyde.

Abstract: A novel monomer of terthiophene with a side chain TEMPO, 4-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetyl-oxy-2,2,6,6-tetramethylpiperidin-1-yloxy (TT-TEMPO) was successfully synthesized. Its corresponding polymer PTT-TEMPO was prepared via electrochemical polymerization on Pt electrode in boron trifluoride diethyl etherate solution. PTT-TEMPO film showed a uniform network structure. Compared with bare Pt electrode, PTT-TEMPO electrode exhibited high electrocatalytic performance for oxidation of benzyl alcohol in the presence of 2,6-lutidine under similar conditions. Benzyl alcohol was selectively oxidized to benzaldehyde based on in situ FTIR analysis.

Keywords: terthiophene, TEMPO, electrochemical polymerization, benzyl alcohol

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Introduction

The stable nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) and its derivatives have received considerable attentions in the past decades, because of their low toxicity, high efficiency and selectivity in oxidation reactions [1-4]. It is well-known that TEMPO can be successfully employed as the catalyst in synthesis of many important compounds including aldehydes [5, 6], nitriles [7, 8] and imines [9, 10] by chemical or electrochemical methods. However, the separation of TEMPO from the reaction solution is difficult, and the TEMPO residue will contaminate the target product [11].

One feasible strategy for solving this issue was to immobilize TEMPO onto solid supports, such as silica [12, 13], carbon nanotubes [14, 15] and graphene oxide [16]. These immobilized TEMPO catalysts were often used for selective oxidation of alcohols, and could be easily separated by centrifugation or filtration. Recently, the electrochemical approach to immobilize TEMPO on the surface of electrode has attracted more and more attention [17, 18]. It could be regarded as a plug-and-play electrode and the separation of TEMPO could be well avoided. The substrate electrode coated with a poly(acrylic acid) film modified with TEMPO was applied for series of alcohol oxidation [19, 20].

Polythiophene, one of the attractive conducting polymers, has been extensively investigated and widely applied in various electrical devices such as sensors, electrochromic devices and solar cells [21-23]. However, the onset oxidation potential of thiophene was relatively high and electrochemical activities of the polymer were unsatisfactory in many cases [24]. One way to solve the problem is to extend the main chain length of thiophene monomer. A terthiophene structure modified with acetic acid was synthesized by Xu and co-workers [25]. Its corresponding polymer possessed good electrochromic performance and redox stability. Owing to its virtues, terthiophene structure might be an ideal backbone for constructing functional polymers [26].

Herein, a novel terthiophene monomer with a side chain TEMPO, 4-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetyl-oxy-2,2,6,6-tetramethylpiperidin-1-yloxy (TT-TEMPO) was synthesized for the first time. The binding force of terthiophene with the side chain TEMPO was quite strong via ester linkage. The corresponding polymer PTT-TEMPO was prepared via electrochemical polymerization and the thickness of the film could be easily controlled with the cycling number [27-29]. The electrocatalytic performance for oxidation of benzyl alcohol was investigated and discussed.

1. Material and methods

1.1 Synthesis of the monomer TT-TEMPO

TT-TEMPO was synthesized by the route displayed in Scheme 1. 3-Thiopheneacetic acid was treated with thionyl chloride ($SOCl_2$), and then reacted with methanol to afford methyl 2-(thiophene-3-yl)acetate. The compound methyl 2-(2,5-di(thiophene-2-yl)thiophene-3-yl)acetate was obtained by the electrophilic bromination procedure using *N*-bromosuccinimide(NBS) as the bromination reagent. Then, 2-(2,5-di(thiophene-2-yl)thiophene-3-yl)acetic acid was prepared via the Suzuki coupling and hydrolysis reaction. The monomer TT-TEMPO was synthesized through esterification reaction of 2-(2,5-di(thiophene-2-yl)thiophene-3-yl)acetic acid with 4-OH-TEMPO using 4-dimethylaminopyridine (DMAP) as the catalyst and dicyclohexylcarbodiimide (DCC) as the dehydrating agent at room temperature. The monomer TT-TEMPO was analyzed in electrospray positive ion mode on a GCT premier (Waters) GC-MS/TOF (time-of-flight).

To characterize the structure of TT-TEMPO by NMR spectroscopy, TT-TEMPO was reduced to TT-TEMPOH using isoascorbic acid according to the reported literature [30]. ^{1}H NMR (500 M, $CDCl_3$) δ: 7.33-7.01 (m, 7H), 5.08 (s, 1H), 3.70 (s, 2H), 1.91 (d, *J*=10.0 Hz, 2H), 1.58 (t, *J*=11.2 Hz, 2H), 1.19 (d, *J*=8.8 Hz, 12H). ^{13}C NMR (125 M, $CDCl_3$) δ: 168.8, 135.3, 134.4, 133.3, 130.5, 129.2, 126.4, 126.3, 125.3, 125.0, 124.8, 123.3, 122.4, 66.1, 57.8, 42.2, 33.7, 30.3. MS (ESI+), m/z, 462.1 $[M+H^+]$.

1.2 Preparation, electrocatalytic performance and characterization of PTT-TEMPO

Electropolymerization experiment was carried out in an undivided cell using a CHI 600e electrochemical analyzer (CH Instrument Inc., USA). A conventional three-electrode system was employed with an "L" type platinum disk electrode (diameter: 3 mm) as the working electrode, a platinum sheet electrode (2.25 cm^2) as the counter electrode, and Ag/Ag^+ electrode (0.1 M $AgNO_3$ in acetonitrile (MeCN) solution) as the reference electrode. PTT-TEMPO was prepared in boron trifluoride diethyl etherate solution (15 mL) containing monomer (0.1 mmol) with anhydrous sodium perchlorate (1.0 mmol) as the supporting electrolyte. The scanning potential was set between 0 and 1.1 V at the scan rate of 25 mV/s. After polymerization, the electrode was washed with MeCN and dried at room temperature. Unless otherwise specified, all electrode potentials reported in this work were quoted to the Ag/Ag^+ electrode.

The electrocatalytic activity of PTT-TEMPO electrode for oxidation of benzyl alcohol was investigated in 15 mL of 0.1 M $NaClO_4$/MeCN solution containing benzyl alcohol (0.5 mmol) and 2,6-lutidine (1.0 mmol). Cyclic voltammetry was carried out between 0 and 0.8 V at the scan rate of 50 mV/s.

PTT-TEMPO was characterized by FTIR using a Nicolet 6700 spectrometer (ThermoFisher, America). The surface morphology of PTT-TEMPO film was characterized using scanning electron microscopy (Zeiss Gemini500).

1.3 In situ FTIR spectroscopic experiment

In situ FTIR spectroscopy experiments were performed on 670 FTIR spectrometer (ThermoFisher, America) equipped with a MCT-A detector cooled by liquid nitrogen. A CaF_2 disk (32 mm * 2 mm) was chosen as the IR window. The Pt disk electrode (d=6 mm) was modified with PTT-TEMPO, and used as the working electrode. Two hundred interferograms were collected at each sample potential, and the spectral resolution was 8 cm^{-1}.

2. Results and discussion

2.1 Characterization of PTT-TEMPO

Fig. 1(A) showed the FTIR spectra of TT-TEMPO and PTT-TEMPO. The peaks appeared at 2974, 2936 and 2858 cm^{-1} in the spectrum (a) were assigned to the methyl and methylene stretching vibration of the monomer TT-TEMPO [31]. The strong intense band appeared at 1731 cm^{-1} was attributed to the C=O stretching vibration and the peak at 1362 cm^{-1} was related to the stretching vibration of N-O• [32, 33]. The peaks at 1236 and 1161 cm^{-1} were attributed to the stretching vibration of acetate C(=O)-O-C [34]. The band at 1460 cm^{-1} was associated with thiophene ring [35]. When the polymer PTT-TEMPO was formed, wavelength shift of some peaks could be observed. Compared with the spectrum of TT-TEMPO, the intensive vibration bands in spectrum (b) at 3102 and 692 cm^{-1} as a result of α-H vibration of thiophene were nearly disappeared [36]. Whereas, the peaks at 3069 and 835 cm^{-1} assigned to β-H vibration were still remained [37]. The new band at 795 cm^{-1} attributed to β-H of thiophene ring appeared in PTT-TEMPO, indicating that α,α'-bonding predominated during electrochemical polymerization of TT-TEMPO [38, 39], as shown in Scheme 2. In addition, the wide peak at 1111 cm^{-1} was possibly caused by doping of ClO_4^- ions into the film during the polymerization process [40]. The band at 1385 cm^{-1} was assigned to the C-C stretching vibration of polymer backbone [35]. With the interference from the bands nearby, the peaks corresponded to the stretching vibration of N-O• and acetate C(=O)-O-C in spectrum (b) were not obviously observed in the spectrum of PTT-TEMPO.

The morphological characterization of PTT-TEMPO film was also studied as shown in Fig. 1 (B). The surface of PTT-TEMPO film displayed a uniform and homogeneous network structure, which may be beneficial to improve its performance.

2.2 Electrochemical performance of PTT-TEMPO electrode

The electrochemical polymerization of TT-TEMPO was performed by cyclic voltammetry. The effect of cycling number on PTT-TEMPO performance was investigated and shown in Fig. 2 (A). Cycle numbers 1, 4, 10 and 15 were chosen as the representatives. The reversible redox peaks centered at about 0.37 V were observed on PTT-TEMPO in 0.1 M $NaClO_4/CH_3CN$ solution. It was corresponded to the one electron transfer process between TEMPO and $TEMPO^+$ [41]. With the increasing of cycling number, the peak current increased gradually, implying the growth of PTT-TEMPO on the surface of working electrode [42].

The electrocatalytic performance of PTT-TEMPO electrode (with cycling number 10) for oxidation of benzyl alcohol in the presence of 2,6-lutidine as the base was performed in 0.1 M $NaClO_4/CH_3CN$ solution at the scan rate of 50 mV/s. As shown in Fig. 2 (B), the typical redox peaks were observed in the blank solution with the oxidation to reduction peak current ratio of about 1.0 (curve a). When benzyl alcohol (0.5 mmol) was added to the solution, only a slight alteration could be observed in curve b. So the electrocatalytic activity of PTT-TEMPO for oxidation of benzyl alcohol was quite low. With the further addition of 2,6-lutidine (1.0 mmol) to the solution, the oxidation peak current increased obviously, while the corresponding current of reduction peak decreased. It showed that the base 2,6-lutidine could accelerate the reaction between $TEMPO^+$ and benzyl alcohol.

For comparison, the voltammetric study of bare Pt electrode for oxidation of benzyl alcohol in the presence of 2,6-lutidine was carried out as shown in curve (d) Fig. 2 (B). On the bare Pt electrode, no redox peaks were observed over the potential range between 0 and 0.8 V. It demonstrated that the oxidation of benzyl alcohol occurs at the surface of PTT-TEMPO electrode instead of the substrate electrode Pt [43].

In order to further demonstrate the efficiency of the PTT-TEMPO electrode, the electrolysis experiment was performed in an undivided cell containing 0.1 M anhydrous $NaClO_4/CH_3CN$ solution (15 mL), benzyl alcohol (0.1 mmol) and 2,6-lutidine (0.2 mmol) at the constant current 6 mA. After being drop-casted with 60 μL ethanol containing 10 v% Nafion, the PTT-TEMPO electrode (2.25 cm^2) was used as the working electrode [17]. The electrolytic reaction was monitored by gas chromatography with peak area normalization method. It was found that benzyl alcohol was selectively converted into benzaldehyde with 91% conversion in 1.5 h.

2.3 In situ FTIR investigation

To further investigation the electrochemical behavior of PTT-TEMPO electrode for oxidation of benzyl alcohol, in situ FTIR spectroscopy was used and the electrode potential was varied from 100 to 800 mV with an interval of 100 mV. The reference potential was 0 mV, and the background noise was subtracted from all the FTIR spectra. When the potentials were more positive than 200 mV, some characteristic peaks appeared and strengthened gradually as shown in Fig. 3 (A). Three negative-going bands at 1647, 1630 and 1586 cm^{-1} were assigned to ring stretching vibration of 2,6-lutidinium cation [44]. The bands at 1280 and 1175 cm^{-1} were related to ring stretching modes and C-H in-plane bending of 2,6-lutidinium cation [45]. It confirmed that 2,6-lutidine received a hydrogen proton to generate 2,6-lutidinium cation. Meanwhile, three important bands at 1702, 1312 and 1204 cm^{-1} were observed clearly, which were attributed to C=O stretching vibration, CHO in-plane bending and C-O stretching vibration of benzaldehyde, respectively [46, 47]. The weak upward band of N-O • stretching vibration was observed at 1362 cm^{-1} [48]. But the corresponding band of N^+=O stretching vibration was not observed with the interference from the bands nearby. Moreover, the band located at 1130 cm^{-1} was assigned to ClO_4^- ions of supporting electrolyte [49].

Another experiment has been carried out to investigate the spectral changes with increasing time at 400 mV. As shown in Fig. 3 (B), the corresponding characteristic bands which were related to benzaldehyde and 2,6-lutidinium cation, were also observed obviously. In addition, the intensity of these bands increased significantly and no new bands emerged with the increasing of time. It showed that the PTT-TEMPO electrode acted as an effective catalyst with high selectively for oxidation of benzyl alcohol in the presence of 2,6-lutidine.

3. Conclusions

We successfully synthesized a novel TEMPO-modified terthiophene monomer TT-TEMPO which was analyzed using FTIR, NMR and MS. The PTT-TEMPO film was obtained by electropolymerization and showed a uniform network structure. It functioned well as the active catalyst for selective oxidation of benzyl alcohol to benzaldehyde in the presence of 2,6-lutidine by the techniques of cyclic voltammetry and in situ FTIR spectroscopy. These basic and explored investigations will lead to further boost this conducting polymer material for other applications such as solar cells and sensors.

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References

[1]. H.A. Beejapur, Q. Zhang, K.C. Hu, L. Zhu, J.L. Wang, Z.B. Ye, ACS Catal. 9 (2019) 2777-2830.

[2]. J.E. Nutting, M. Rafiee, S.S. Stahl, Chem. Rev. 118 (2018) 4834-4885.

[3]. K. Lagerblom, P. Wrigstedt, J. Keskiväli, A. Parviainen, T. Repo, ChemPlusChem 81 (2016) 1160-1165.

[4]. J.M. Hoover, S.S. Stahl, J. Am. Chem. Soc. 133 (2011) 16901-16910.

[5]. J.M. Hoover, J.E. Steves, S.S. Stahl, Nat. Protoc. 7 (2012) 1161-1166.

[6]. A. Badalyan, S.S. Stahl, Nature 535 (2016) 406-410.

[7]. L.M. Dornan, Q. Cao, J.C.A. Flanagan, J.J. Crawford, M.J. Cook, M.J. Muldoon, Chem. Commun. 49 (2013) 6030-6032.

[8]. Q.G. Chen, C.J. Fang, Z.L. Shen, M.C. Li, Electrochem. Commun. 64 (2016) 51-55.

[9]. B. Huang, H.W. Tian, S.S. Lin, M.H. Xie, X.C. Yu, Q. Xu, Tetrahedron Lett. 54 (2013) 2861-2864.

[10]. Z.Z. Hu, F.M. Kerton, Org. Biomol. Chem. 10 (2012) 1618-1624.

[11]. J. Tang, Q. Zhang, K.C. Hu, P. Zhang, J.L. Wang, J. Catal. 353 (2017) 192-198.

[12]. A.J. Shakir, C. Paraschivescu, M. Matache, M. Tudose, A. Mischie, F. Spafiu, P. Ionita, Tetrahedron Lett. 56 (2015) 6878-6881.

[13]. Y.J. Liu, X.P. Wang, W.G. Song, G.W. Wang, Polym. Chem. 6 (2015) 7514-7523.

[14]. W. Yu, M.H. Zhou, T.Q. Wang, Z.D. He, B.Y. Shi, Y. Xu, K. Huang, Org. Lett. 19 (2017) 5776-5779.

[15]. Y.M. Wang, X.Y. Song, S.H. Shao, H.M. Zhong, F. Lin, RSC Adv. 2 (2012) 7693-7698.

[16]. A.J. Shakir, D.C. Culita, J. Calderon-Moreno, A. Musuc, O. Carp, G. Ionita, P. Ionita. Carbon 105 (2016) 607-614.

[17]. A. Das, S.S. Stahl, Angew. Chem. Int. Ed. 56 (2017) 8892-8897.

[18]. D.P. Hickey, R.D. Milton, D. Chen, M.S. Sigman, S.D. Minteer. ACS Catal. 5 (2015) 5519-5524.

[19]. Y. Kashiwagi, T. Osa, Chem. Lett. 22 (1993) 677-680.

[20]. S.Y. Kishioka, S. Ohki, T. Ohsaka, K. Tokuda, J. Electroanal. Chem. 452 (1998) 179-186.

[21]. D.B. Kamble, A.K. Sharma, J.B. Yadav, V.B. Patil, R.S. Devan, A.A. Jatratkar, M.A. Yewale, V.V. Ganbavle, S.D. Pawar, Sensors Actuat. B-Chem. 244 (2017) 522-530.

[22]. M.E. Nicho, H.L. Hu, C. López-Mata, J. Escalante, Sol. Energ. Mat. Sol. C. 82 (2004) 105-118.

[23]. M. Lanzi, E. Salatelli, L. Giorgini, M. Marinelli, F. Pierini, Polymer 149 (2018) 273-285.

[24]. J. Hwang, J.I. Son, Y.B. Shim, Sol. Energ. Mat. Sol. C. 94 (2010) 1286-1292.

[25]. Y.S. Zhang, B.Y. Lu, L.Q. Dong, H. Sun, D.F. Hu, H.K. Xing, X.M. Duan, S. Chen, J.K. Xu, Electrochimi. Acta 220 (2016) 122-129.

[26]. R. Jamal, Y. Osman, A. Rahman, A. Ali, Y. Zhang, T. Abdiryim, Materials 7 (2014) 3786-3801.

[27]. M. Raicopol, C. Andronescu, R. Atasiei, A. Hanganu, L. Pilan, J. Electrochem. Soc. 161 (2014) 103-113.

[28]. J.B. Zhang, Y. Hao, L. Yang, H. Mohammadi, N. Vlachopoulos, L.C. Sun, A. Hagfeldt, E. Sheibani, Electrochimi. Acta 300 (2019) 482-488.

[29]. F. Li, Y.P. Zhang, S.R. Kwon, J.L. Lutkenhaus, ACS Macro. Lett. 5 (2016) 337-341.

[30]. Y. Ba, E.V. Mathias, US 2008/0318907 A1, 2008-12-25.

[31]. T. Siu, S. Yekta, A.K. Yudin, J. Am. Chem. Soc. 122 (2000) 11787-11790.

[32]. M. Tjahjono, S.Y. Cheng, C.Z. Li, M. Garland, J. Phys. Chem. A 114 (2010) 12168-12175.

[33]. M. Aydın, B. Esat, Ç. Kılıç, M.E. Köse, A. Ata, F. Yılmaz, Eur. Polym. J. 47 (2011) 2283-2294.

[34]. W. Kasai, T. Kondo, Macromol. Biosci. 4 (2004) 17-21.

[35]. C. Kvarnström, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, Electrochimi. Acta 44 (1999) 2739-2750.

[36]. T. Abdiryim, C.B. Zhao, R. Jamal, A. Ubul, W. Shi, I. Nurulla, Polym. Sci. Ser. B 54 (2012) 413-419.

[37]. T. Abdiryim, R. Jamal, A. Ubul, I. Nurulla, Molecules 17 (2012) 8647-8660.

[38]. D.H. Zhang, J.G. Qin, G. Xue, Synth. Met. 100 (1999) 285-289.

[39]. X. Hu, L.G. Xu, Polym. 41 (2000) 9147-9154.

[40]. A. Benyoucef, F. Huerta, J.L. Vázquez, E. Morallon, Eur. Polym. J. 41 (2005) 843-852.

[41]. M.F. Semmelhack, C.S. Chou, D.A. Cortes, J. Am. Chem. Soc. 105 (1983) 4492-4494.

[42]. L.Y. Xu, J.S. Zhao, R.M. Liu, H.T. Liu, J.F. Liu, H.S. Wang, Electrochimi. Acta 55 (2010) 8855-8862.

[43]. J.J. Lu, J.Q. Ma, J.M. Yi, Z.L. Shen, Y.J. Zhong, C.A. Ma, M.C. Li, Electrochimi. Acta 130 (2014) 412-417.

[44]. S.N. Timmiati, A.A. Jalil, S. Triwahyono, H.D. Setiabudi, N.H.R. Annuar, Appl. Catal. A: Gen. 459 (2013) 8-16.

[45]. M.L. Wang, Y.Y. Zhang, Q.J. Xie, S.Z. Yao, Electrochimi. Acta 51 (2005) 1059-1068.

[46]. D.M. Meier, A. Urakawa, A. Baiker, J. Phys. Chem. C 113 (2009) 21849-21855.

[47]. C. Keresszegi, D. Ferri, T. Mallat, A. Baiker, J. Phys. Chem. B 109 (2005) 958-967.

[48]. T. Kurosaki, K.W. Lee, M. Okawara, J. Polym. Sci. Part A: Pol. Chem. 10 (1972) 3295-3310.

[49]. R.M. Souto, J.L. Rodríguez, E. Pastor, T. Iwasita, Langmuir 16 (2000) 8456-8462.

Fig. 1. (A) FTIR spectra of TT-TEMPO (a) and PTT-TEMPO (b). (B) SEM image of PTT-TEMPO film.

Fig. 2. (A) Cyclic voltammograms of PTT-TEMPO electrode (prepared with different cycling numbers 1, 4, 10 and 15) in 0.1 M $NaClO_4/CH_3CN$ solution. (B) Cyclic voltammograms of PTT-TEMPO electrode (with cycling number 10) in 0.1 M $NaClO_4/CH_3CN$ solution (a); with benzyl alcohol (0.5 mmol) (b); with benzyl alcohol (0.5 mmol) + 2,6-lutidine (1.0 mmol) (c); Cyclic voltammogram of bare Pt electrode in 0.1 M $NaClO_4/CH_3CN$ solution with benzyl alcohol (0.5 mmol) + 2,6-lutidine (1.0 mmol) (d).

Fig. 3. (A) In situ FTIR spectra collected on PTT-TEMPO electrode during the oxidation of benzyl alcohol in the presence of 2,6-lutidine in 0.1 M $NaClO_4/CH_3CN$ solution at potentials varied from 100 to 800 mV. (B) In situ time-resolved FTIR spectra collected on PTT-TEMPO electrode during the oxidation of benzyl alcohol in the presence of 2,6-lutidine in 0.1 M $NaClO_4/CH_3CN$ solution at 400 mV.

Scheme 1. Synthesis of the monomer TT-TEMPO.

Scheme 2. Electrochemical polymerization of the monomer TT-TEMPO.