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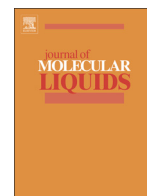
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Electrosynthesis of high-density polythiophene nanotube arrays and their application for sensing of riboflavin



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ABSTRACT

High-density arrays of polythiophene nanotubes were successfully prepared through electrochemical polymerization of the monomer in the pores of porous anodic alumina (PAA) template. The resultant polymeric tubular structures were identified by the field-emission scanning electron microscopy with a diameter of the order of ca 100 nm and a length of up to several micrometers. Different characterizations, including SEM, TEM and EDS, were employed to prove that conducting polythiophene nanotubes were synthesized successfully by this facile method. The synthesized polythiophene nanotubes were employed for proposing a new electrochemical sensor for Riboflavin (RF). Under optimal conditions, the suggested sensor could be used for determination of RF ranging from 0.01 to 65 μM with a low detection limit of 3 nM. The prepared sensor possessed accurate and rapid response to RF and good sensitivity, stability and repeatability. Furthermore it showed an average recovery of 97% in human plasma.

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1. Introduction

π -conjugated conductive polymers, also known as “synthetic metals”, have attracted considerable attention in both fundamental and applied studies, and through the last few decades a tremendous amount of research has been carried out in the field of conductive polymers [1,2]. So, the Nobel Prize in Chemistry has been awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa in 2000 for the discovery and development of conductive polymers [3].

Due to their special electrical, chemical and optical properties, light weight, redox activity and their processability, a variety of conductive polymers (e.g., polyacetylenes, polyanilines, polypyrroles, poly(p-phenylene-vinylene) and polythiophenes), especially their nanotubular structure, have garnered special attention due to the unique combination of electronic properties of conducting polymers and large surface area of nanotubes [3–8].

Among the conductive polymers, polythiophenes (PTs) have received great interest over the past few years due to their flexibility, ease of doping and good thermal and electrical stability that lead to some unique advantages of PTs for development of various applications. PTs have been studied for various applications, including organic field effect transistor, solar cells, supercapacitors, sensors, electrochromic devices and light emitting diodes [6,9,10].

“Template synthesis method” is one of the most effective methods for synthesis of nanoscale conjugating tubular polymers. Conductive polymer nanotubes have been synthesized chemically or electrochemically in the pores of a template. Electrochemical deposition in the pores of the template has attracted a good deal of research interest because with this method it is easy to control the length, diameter, shape and structural properties of nanotubes [11–13].

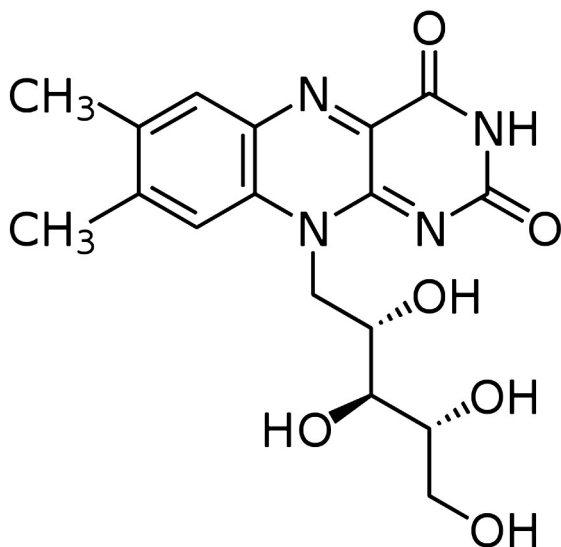
In this study we report the template electrosynthesis and characterization of polythiophene nanotubes, and sensing application of them toward riboflavin, since the performance of sensors and biosensors can be improved by using nanomaterials [14–19].

Vitamin B₂, also called riboflavin (RF), is one of the essential water soluble vitamins (the chemical structure is shown in Scheme 1). RF plays very important roles in living organisms, especially via its contribution towards the formation of two flavin coenzymes: flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD) [20,21]. In addition to energy production for the body by conversion of carbohydrates into glucose, RF also plays a key role in promoting growth, immunity, cell regeneration, antioxidation and cancer prevention [22,23].

The determination of trace amounts of RF is essential for the quality control of feed and pharmaceuticals. Several analytical methods have been developed for determination of RF due to its biological significance. These methods include liquid chromatography [24,25], chemiluminescence [26], spectrophotometry [27], fluorescence [28] and electrochemical methods [29]. Among these methods, electrochemical techniques have the advantages of high sensitivity and selectivity and also being inexpensive [30].

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Scheme 1. The chemical structure of riboflavin.

However, there are only few reports on applying electroanalytical methods in the determination of RF [29,31,32], usually involving adsorptive stripping voltammetry at mercury electrodes under basic conditions [33,34].

To the best of our knowledge, nanostructured conducting polymers have never been used for modification of glassy carbon (GC) electrode for RF determination. Therefore, in this study we used conductive polymer nanotubes for GC electrode modification which exhibited very good activity towards RF detection and determination.

2. Experimental

Conducting polythiophene nanotubes were synthesized through electrochemical polymerization method using nonporous PAA template, which was purchased from Whatman Co.

2.1. Materials

PAA membranes (Anodisc 13 with 100 nm pore diameter) were purchased from Whatman (UK). Acetonitrile was purchased from Merck and was used after drying with molecular sieves under argon atmosphere. All other chemicals not mentioned here were of analytical reagent grade and were used as received. All the voltammetric studies were carried out at room temperature (25 ± 0.1 °C) in 0.04 M Britton Robinson (BR) buffer, prepared from acetic acid, phosphoric acid and boric acid. The solutions were prepared in deionized water and deoxygenated by bubbling high purity (99.99%) nitrogen gas through them for 15 min prior to the experiments. A stock solution of 0.01 mM riboflavin was prepared before use and protected from light with aluminum foil.

2.2. Apparatus

Electrochemical measurements were performed with a μ -Autolab electrochemical system (Eco Chemie, Ultec, The Netherlands), equipped with NOVA software (upgrade 1.7). A conventional three-electrode cell was employed for all electrochemical experiments incorporating a KCl-saturated Ag/AgCl reference electrode and a platinum counter electrode.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis were performed using a FEI Quanta 250 FEG. A transmission electron microscope (TEM) image was taken with a Zeiss LEO 912 Omega operating at 80 kV.

2.3. Preparation of polythiophene nanotubes (PTN)

Before electropolymerization of thiophene, a thin layer of 70 nm gold was sputtered on one side of the PAA membranes to make the surface electrically conductive and serve as working electrode during electrodeposition.

Conductive polythiophene nanotubes (PTN) were prepared by electrochemical polymerization of thiophene in a three electrode system. They were fabricated by potentiostatic electropolymerization of monomer at 1.4 V versus Ag/AgCl in an acetonitrile solution of 25 mM thiophene and 100 mM tetrabutylammonium perchlorate. After electropolymerization, the membrane had a dark brown color indicative of the formation of PTNs.

2.4. Modified electrode preparation

The fabrication of modified GC electrode is summarized as follows: after electropolymerization, PAA templates was rinsed with deionized water and dissolved in 1 M NaOH etching solution, then washed several times by deionized water and ethanol and then dispersed in 10 ml ethanol and ultrasonicated for 5 min to get a dark brown homogeneous solution (0.5 mg/ml). The resulting PTNs were examined for modification of GC electrode. The bare GC electrodes (2 mm diameter) were carefully polished with alumina slurry (0.05 μ m) on a polishing cloth and sonicated successively in deionized water and ethanol.

A 0.2-wt.% chitosan solution was prepared by dissolving 20 mg of chitosan flakes into 10 ml of 1.0% acetic acid and stirred for 3 h at room temperature until complete dissolution.

The GC electrodes were treated by dropping a suspension (10 μ l) of the homogeneously dispersed PTN–ethanol solution and 5 μ l of the chitosan solution on the surface of the cleaned electrode (the effect of PTN amount on the sensing performance was also investigated. For this purpose different amounts of homogeneous PTN solution (2 to 20 μ l) were dropped on the electrode surface. With regard to the sensor performance, 10 μ l has been chosen as the optimized value). Then, modified electrodes were dried in air to form a PTN film on the electrode surface. The prepared electrodes are denoted as PTN/GC electrode and were employed for electrochemical sensing of RF.

2.5. SEM and TEM sample preparation

The structure of PTNs grown in PAA template was investigated by SEM and TEM. To obtain SEM images of PTNs, a piece of the PAA template embedded with PTNs was fixed to a specimen mount. 1 ml of NaOH 1.0 M was dropped on the surface of the sample to partially dissolve the template, and then they were rinsed with water and ethanol for several times. Another SEM sample was prepared by completely dissolving the template in the solution containing 1.0 M NaOH. Nanotubes are then washed several times by deionized water and ethanol. The specimen for TEM was also prepared by completely dissolving the PAA template in 1.0 M NaOH. The residual nanotubes were carefully rinsed with deionized water and ethanol and then dispersed into ethanol solution via ultrasonication. A copper grid was dipped into the solution and then dried before TEM measurement.

3. Results and discussion

3.1. Morphology and structure of PTNs

The SEM images of as-prepared structures which are displayed in Fig. 1 confirm the formation of nanotubes and show uniform cylindrical nanotubes with a high aspect ratio. A top view SEM micrograph of the synthesized PTN after partial etching of the PAA template in 1.0 M NaOH is displayed in Fig. 1a. From this image one can see the well packed nanotube arrays with the diameter of about 100 nm standing perpendicular to PAA template. PTNs in the pores of PAA template

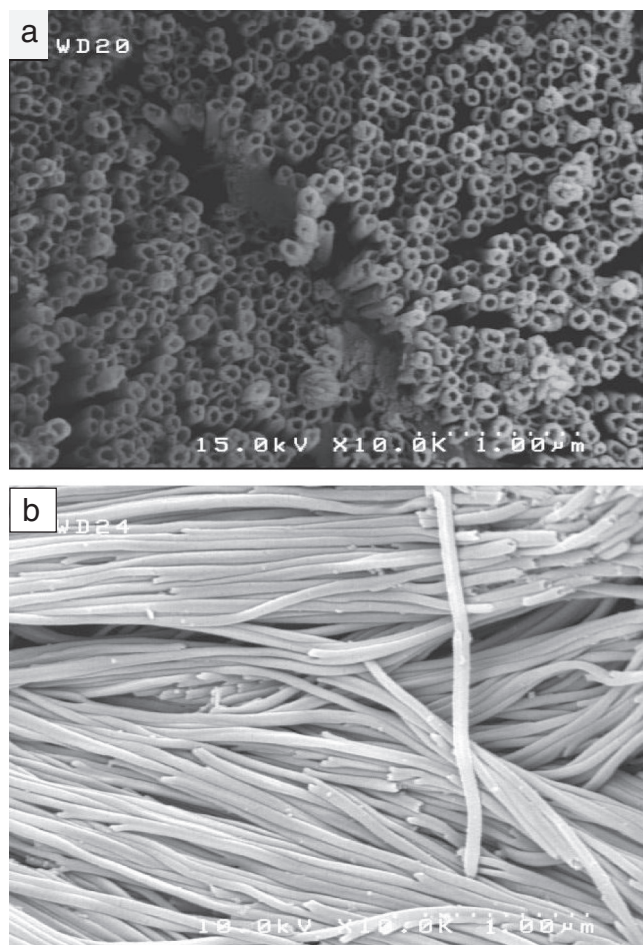


Fig. 1. (a) SEM image of polythiophene nanotubes (PTNs), (b) SEM image of the nanotubes released from the template.

possess high density which suggests that the electrodeposition of thiophene in the PAA template is efficient.

Fig. 1b shows the SEM image of the PTNs released from the PAA template with about 100 nm in diameter and several microns in length. The diameter of all nanotubes is almost the same, which corresponds to the pore diameter of the PAA membranes. These results demonstrate that the PTNs can grow in the nano-pores of the PAA membrane.

To confirm the composition of synthesized PTNs, EDS analysis was performed (Fig. 2). As can be expected, the polymerized product is composed of C and S elements with 61.05 and 20.22 weight percent respectively. In addition, the spectrum shows also Al and O peaks with weight percent of 8.12 and 10.61 respectively. It can be attributed to the presence of alumina which remains after dissolving of the PAA membrane.

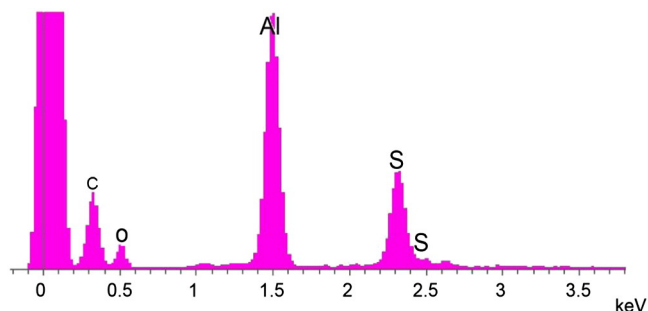


Fig. 2. Energy dispersive analysis (EDS) of polythiophene nanotubes.

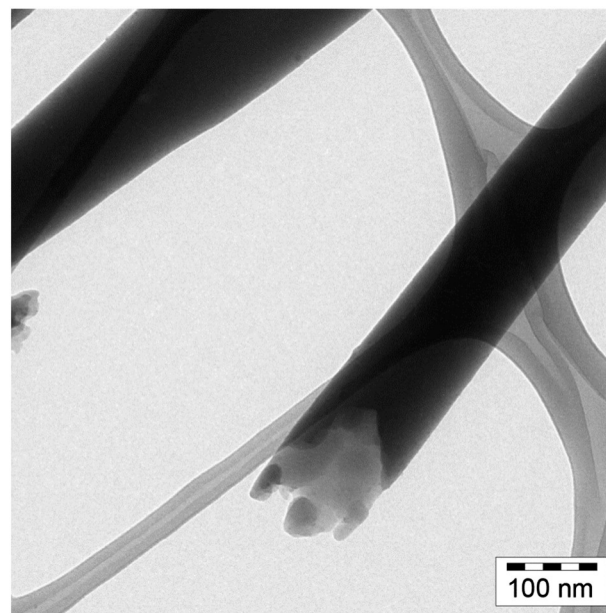


Fig. 3. TEM image of synthesized PTNs.

Fig. 3 shows a TEM image of PTNs. This image shows the presence of PTNs of about 100 nm which is corresponded to SEM results.

3.2. Voltammetric response of PTN/GC electrode to RF

Cyclic voltammograms (CVs) of modified and unmodified electrodes were recorded in electrolyte solution (25 ml of 0.04 M BR buffer) and results are shown in Fig. 4. Voltammograms 'a' and 'b' correspond to the voltammetric behavior of PTN/GC electrode in the absence and presence of riboflavin respectively, while voltammogram 'c' corresponds to the voltammetric behavior of the GC electrode in the presence of riboflavin (8 μ M of riboflavin). As can be observed in the CVs, no obvious redox peak can be observed for the modified electrode in whole scanning potential ranges in pure BR solution (curve a).

When the RF was added to BRS a well-defined redox peak appeared for the modified electrode (curve b). This peak corresponds to the redox behavior of 8 μ M RF in BR buffer and is higher than that of bare GC electrode (curve c) and also has less negative reduction and oxidation

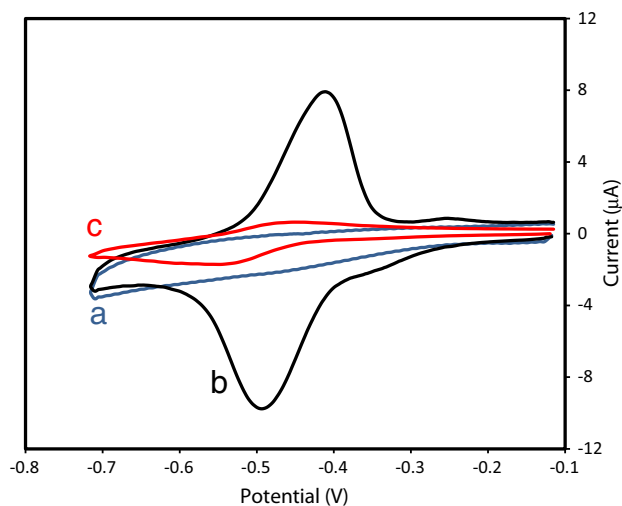
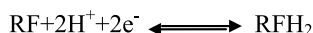


Fig. 4. CVs of (a) PTN/GC electrode in pure BR solution, (b) PTN/GC electrode in BR solution containing 8 μ M RF (pH = 7), and (c) bare GC electrode in BR solution containing 8 μ M RF. Scan rate of 100 mV/s.

potentials. The large surface-to-volume ratio of the PTNs increases the electroactive area and consequently, the PTN/GC electrode is more sensitive than the bare electrode for RF assay and could be used for the direct determination of RF.

3.3. Effect of pH

The effect of pH on voltammetric response of PTN/GC electrode on detection and determination of RF was studied. Cyclic voltammograms of 8 μM solution of RF were recorded in 0.04 M BR buffer solution over a pH range from 2.0 to 12.0 and are shown in Fig. 5a. As it is obvious from this figure, the anodic peak currents for RF in the pH range of 2–7 are almost the same. However, in alkaline solutions RF degradation occurs and the peak current decreases [35]; the peak potential for anodic peak shifted to the negative potentials by increasing pH values. This is expected because of the participation of protons in the oxidation process (as shown in following equation) [33]:



The oxidation peak potential (E'_{ox}) is given by:

$$E'_{\text{ox}} = E_{\text{ox}} - (2.303 mRT/2F)p\text{H}$$

where m is the number of protons involved in the reaction, E_{ox} is the oxidation peak potential at $\text{pH} = 0.0$, and R , T and F have their usual meanings. The values of E'_{ox} as a function of solution's pH are plotted

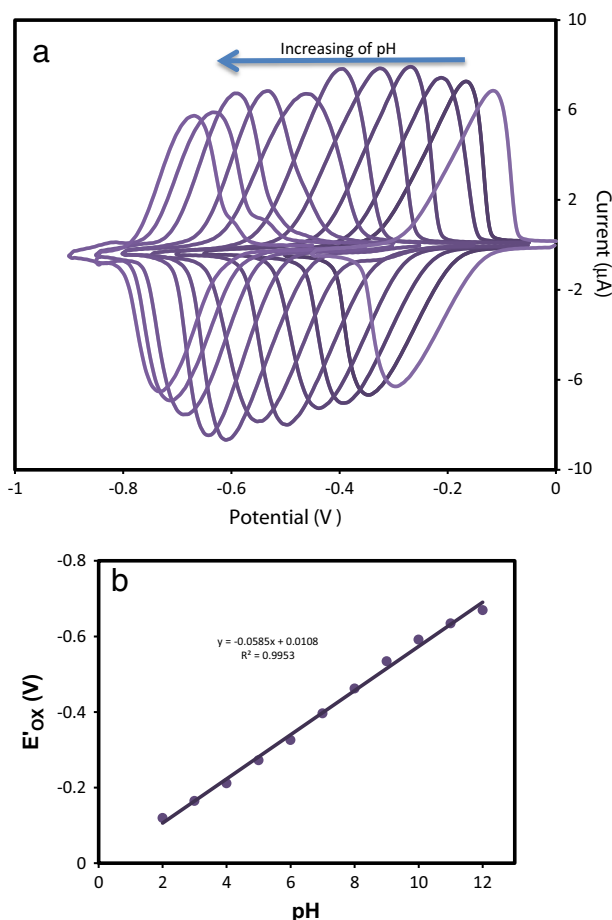


Fig. 5. (a) CVs of PTN/GC electrode for 8 μM RF at different pH values (from right to left: 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0), (b) variation of oxidation potential (E'_{ox}) of RF as a function of pH (scan rate of 100 mV/s).

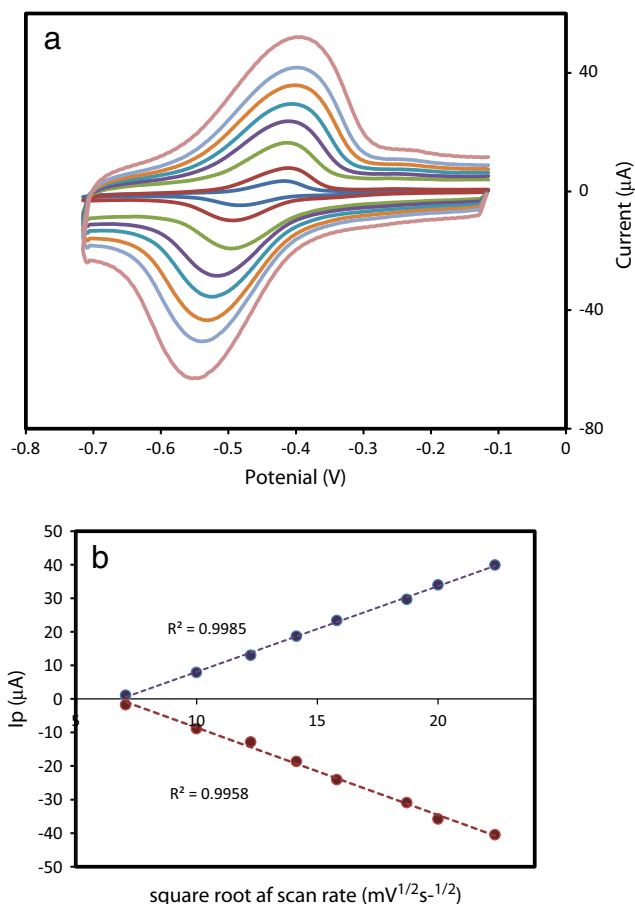


Fig. 6. (a) CVs of PTN/GC electrode in 0.04 M BRS ($\text{pH} = 7.0$) containing 30 μM RF at different scan rates (from the bottom: 50, 100, 150, 200, 250, 350, 400 and 500 mV/s); (b) dependence of current vs. square root of scan rate for anodic and cathodic peaks.

in Fig. 5b. It was observed that the values of E'_{ox} decreased linearly with pH in the range of 2.0–12.0 with a slope of 58.5 mV/pH, which corresponds to the theoretical one for a reversible, two-proton coupled with a two-electron redox reaction process [36]. These results confirm the above-mentioned electrochemical reaction for RF.

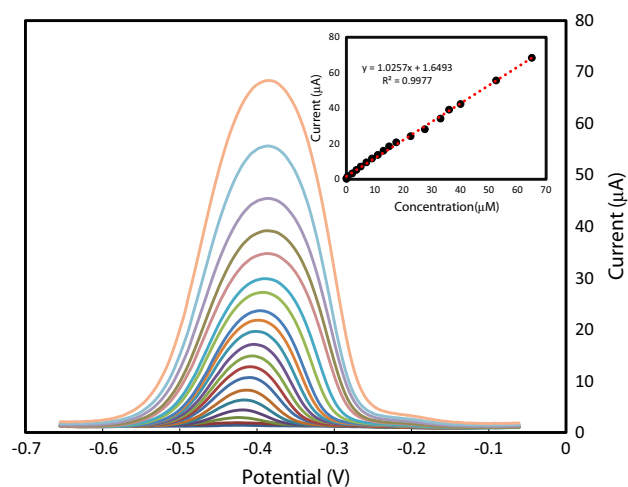


Fig. 7. DPV of PTN/GC electrode for different concentrations of RF in 0.04 M BRS ($\text{pH} = 7.0$, scan rate of 100 mV/s); concentrations from bottom to top: 0.01, 0.05, 0.5, 2, 3.5, 5, 7, 9, 11, 13, 15, 17.5, 22.5, 27.5, 33, 36, 40, 52.5 and 65 μM .

Table 1
Comparison between some methods for electrochemical determination of RF.^a Squarewave voltammetry.

Method	Electrolyte	Sensitivity	Linear range	Detection limit (M)
Voltammetry [29]	0.05 M PBS pH 7.0	769 $\mu\text{A}/\text{mM}$	0.4–1 μM	2×10^{-8}
Voltammetry [37]	0.01 M Na_2SO_4 pH 2.0		0.11–1 μM , 0.8–110 nM	1×10^{-10}
Voltammetry [38]	0.1 M PBS pH 4.0	1.5705 $\mu\text{A}/\mu\text{M}$	50–200 μM	5×10^{-8}
SWV ^a [33]	0.2 M PBS pH 7.0	–	0.010–0.07, 0.07–1 μM	5×10^{-9} at 72 °C
DPV [39]	Breast milk pH 6		–	2×10^{-8}
DPV [23]	0.1 M PBS pH7	2.8 $\mu\text{A}/\mu\text{M}$	0.03–500 μM	5×10^{-9}
Voltammetry (this study)	0.04 M BRS (pH = 7)	1.0257 $\mu\text{A}/\mu\text{M}$	0.01–65 μM	3×10^{-9}

^a Squarewave voltammetry.

3.4. Effect of scan rate

The effect of scan rate on the voltammetric response of the PTN/GC electrode at different scan rates for 8 μM RF in BR buffer (0.04 M, pH = 7.0) is shown in Fig. 6a. It can be observed that anodic and cathodic peak currents are increased by increasing scan rate in the range of 50–500 mV/s. Also for more investigations, the values of anodic and cathodic peak currents versus square root of scan rates were plotted and shown in the Fig. 6b. This plot shows a linear relationship between peak currents and square root of scan rate, for both anodic and cathodic suggesting that the reaction of RF on PTN/GCE is a diffusion controlled process, which is an ideal case for quantitative measurements.

3.5. Electrochemical determination of RF

We also examined the electrochemical response of PTN/GC electrode by changing the concentration of RF (Fig. 7), using differential pulse voltammetry (DPV) technique because of the better sensitivity of this technique compared with CV. The RF oxidation currents increased with increasing of the RF concentration. The inset of Fig. 7 shows the calibration curve of the PTN/GC electrode which gives a linear response towards RF with good correlation coefficients of 0.9977. The modified GC electrode had a sensitivity of 1.0257 $\mu\text{A}/\mu\text{M}$, in the concentration range of 0.01–65 μM , and possessed a detection limit of 3 nM (signal-to noise ratio of 3). The efficient electrocatalytic property of PTN/GC electrode to RF could be attributed to the large catalytically electroactive surface area of nanotubes.

The percent relative standard deviation (%RSD = $100 \times [(\text{standard deviation of array Y}) / (\text{average of array Y})]$) for 10 μM RF by using ten fresh modified electrode obtained 4.3%, which shows high repeatability of the electrode modification method.

The stability of the PTN/GC electrode was also investigated after electrode storage in BR buffer solution at room temperature for three weeks. The response of the modified electrode lost approximately 4.6% of its original response for RF. Thus, the suggested electrode showed a good repeatability and high stability.

The performance of the prepared modified electrode is compared with previously reported modified electrodes for RF determination (Table 1). The modified electrode in this work overall is appropriate and favorable for RF detection and determination. Compared with the other reported sensors, the proposed sensor works at mild conditions

(pH7) without using toxic mercury drop electrode, has wide linear response range (0.01–65 μM), high sensitivity (1.0257 $\mu\text{A}/\mu\text{M}$), low detection limit (3 nM) and high repeatability and stability. These all make the presented sensor in this research comparable with previous studies.

3.6. Interference studies

Before evaluating the sensor for analysis of RF in real samples, the interference studies were carried out with several species. The limit of the interfering substances was defined as error less than 3% in determination of 5 μM of RF concentration. Various common metal ions, vitamins and other organic compounds were examined here. The results showed no serious interference by 100-fold excess of Na^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , and 20-fold excess of folic acid, uric acid, ascorbic acid, vitamin B₁, vitamin B₆ and vitamin B₁₂.

3.7. Determination of RF in human plasma

In order to show the practical application of the developed sensor, experiments were performed to determine the concentration of RF in human plasma. The plasma samples were diluted with BRS (0.04 M, pH = 7.0) and analysis was performed by the standard addition technique. The results which are listed in Table 2 show an average recovery of 97%, suggesting the high accuracy of PTN based sensor. According to these results the proposed sensor provides a good alternative to determine RF in multivitamin tablets with high accuracy.

4. Conclusions

In this work, a new RF sensor was fabricated on the basis of GC electrode modified with PTNs. An electrochemical method was employed for the controlled synthesis of high density arrays of polythiophene nanotubes in the PAA template. After dissolving the template, the prepared nanotubes were dispersed in ethanol and were employed for modification of GC electrode. The PTNs were characterized by SEM, TEM, and EDS analyses and the modified electrodes were characterized by CV and DPV. These results show a well-defined response and also a stable and efficient catalytic property of the PTN modified GC electrode for RF determination.

The proposed electrochemical sensor allows sensitive and selective nanomolar determination of RF in the presence of various potentially interfering substances. The method provides a useful tool for very sensitive and accurate determination and quantification of Riboflavin in human plasma.

Acknowledgments

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Table 2
Determination and recovery test for RF in human blood plasma.

Spiked (μM)	Found ^a (μM)	Recovery (%)
0.0	0.01	–
2.0	1.91 \pm 0.07	95.0
5.0	4.91 \pm 0.10	98.0
10.0	9.81 \pm 0.11	98.0

^a Mean \pm standard deviation ($n = 3$).

References

- [1] G.-F. Wang, X.-M. Tao, J. Xin, B. Fei, *Nanoscale Res. Lett.* 4 (2009) 613–617.
- [2] R. Jain, D.C. Tiwari, P. Karolia, *J. Mol. Liq.* 196 (2014) 308–313.
- [3] X. Lu, W. Zhang, C. Wang, T.-C. Wen, Y. Wei, *Prog. Polym. Sci.* 36 (2011) 671–712.
- [4] X. Zou, S. Zhang, M. Shi, J. Kong, *J. Solid State Electrochem.* 11 (2007) 317–322.
- [5] Y.-Z. Long, M.-M. Li, C. Gu, M. Wan, J.-L. Duvail, Z. Liu, Z. Fan, *Prog. Polym. Sci.* 36 (2011) 1415–1442.
- [6] M.R. Karim, K.T. Lim, C.J. Lee, M.S. Lee, *Synth. Met.* 157 (2007) 1008–1012.
- [7] T.M. Nguyen, S. Lee, S.B. Lee, *Nanomedicine* (2014), <http://dx.doi.org/10.2217/nnm.13.153>.
- [8] R. Xiao, S.I. Cho, R. Liu, S.B. Lee, *J. Am. Chem. Soc.* 129 (2007) 4483–4489.
- [9] J.-H. Kim, M. Kim, H. Jinnai, T.J. Shin, H. Kim, J.H. Park, S.B. Jo, K. Cho, *ACS Appl. Mater. Interfaces* 6 (2014) 5640–5650.
- [10] A. Laforgue, P. Simon, C. Sarrazin, J.-F. Fauvarque, *J. Power Sources* 80 (1999) 142–148.
- [11] S.I. Cho, S.B. Lee, *Acc. Chem. Res.* 41 (2008) 699–707.
- [12] A. Hajian, A. Rafati, A. Afraz, M. Najafi, *J. Electrochem. Soc.* 161 (2014), <http://dx.doi.org/10.1149/2.0881409jes>.
- [13] M. Fu, Y. Zhu, R. Tan, G. Shi, *Adv. Mater.* 13 (24) (2001) 1874–1877.
- [14] A. Afraz, A. Rafati, A. Hajian, *J. Solid State Electrochem.* 17 (2013) 2017–2025.
- [15] A. Rafati, A. Afraz, A. Hajian, P. Assari, *Microchim. Acta* (2014), <http://dx.doi.org/10.1007/s00604-014-1293-7>.
- [16] A. Salimi, R. Hallaj, *J. Solid State Electrochem.* 16 (2012) 1239–1246.
- [17] A.A. Rafati, A. Afraz, *Mater. Sci. Eng. C* 39 (2014) 105–112.
- [18] H. Bagheri, A. Afkhami, A. Shirzadmehr, H. Khoshafar, *J. Mol. Liq.* 197 (2014) 52–57.
- [19] M. Najafi, L. Maleki, A.A. Rafati, *J. Mol. Liq.* 159 (2011) 226–229.
- [20] I. Caelen, A. Kalman, L. Wahlström, *Anal. Chem.* 76 (2003) 137–143.
- [21] A. Kundu, S. Nandi, R.K. Layek, A.K. Nandi, *ACS Appl. Mater. Interfaces* 5 (2013) 7392–7399.
- [22] S.B. Revin, S.A. John, *Electrochim. Acta* 75 (2012) 35–41.
- [23] B. Kaur, R. Srivastava, *Electroanalysis* 26 (2014) 1078–1089.
- [24] M.-J. Esteve, R. Farré, A. Frígola, J.-M. García-Cantabella, *J. Agric. Food Chem.* 49 (2001) 1450–1454.
- [25] P. Jin, L. Xia, Z. Li, N. Che, D. Zou, X. Hu, *J. Pharm. Biomed. Anal.* 70 (2012) 151–157.
- [26] M. Wang, L. Zhao, M. Liu, J.-M. Lin, *Spectrochim. Acta A* 66 (2007) 1222–1227.
- [27] A. Niazi, J. Zolgharnein, S. Afuni-Zadeh, *Anal. Sci.* 23 (2007) 1311–1316.
- [28] V. León-Ruiz, S. Vera, M.P. San Andrés, *Anal. Bioanal. Chem.* 381 (2005) 1568–1575.
- [29] J. Bai, J. Ndamaniha, L. Liu, L. Yang, L. Guo, *J. Solid State Electrochem.* 14 (2010) 2251–2256.
- [30] R.M. Kotkar, P.B. Desai, A.K. Srivastava, *Sensor Actuators B Chem.* 124 (2007) 90–98.
- [31] A. Economou, P.R. Fielden, *Electroanalysis* 7 (1995) 447–453.
- [32] L.S. Anisimova, E.V. Mikheeva, V.F. Slipchenko, *J. Anal. Chem.* 56 (2001) 658–662.
- [33] S.-H. Wu, J.-J. Sun, Z.-B. Lin, A.-H. Wu, Y.-M. Zeng, L. Guo, D.-F. Zhang, H.-M. Dai, G.-N. Chen, *Electroanalysis* 19 (2007) 2251–2257.
- [34] J. Wang, D.B. Luo, P.A.M. Farias, J.S. Mahmoud, *Anal. Chem.* 57 (1985) 158–162.
- [35] S. Berchmans, R. Vijayavalli, *Langmuir* 11 (1995) 286–290.
- [36] D. Nematollahi, Z. Zohdijamil, H. Salehzadeh, *J. Electroanal. Chem.* 720–721 (2014) 156–161.
- [37] A. Safavi, N. Maleki, H. Ershadifar, F. Tajabadi, *Anal. Chim. Acta.* 674 (2010) 176–181.
- [38] H. Zhang, J. Zhao, H. Liu, H. Wang, R. Liu, J. Liu, *Int. J. Electrochem. Sci.* 5 (2010) 295–301.
- [39] E.V. Mikheeva, O.A. Martynyuk, G.B. Slepchenko, L.S. Anisimova, *J. Anal. Chem.* 64 (2009) 731–734.