Electrospun Ru(bpy)₃²⁺-doped nafion nanofibers for electrochemiluminescence sensing

Cuisong Zhou, Zhen Liu, Jianyuan Dai and Dan Xiao*

Electrospun $Ru(bpy)_3^{2+}$-doped Nafion (ERDN) nanofibers were successfully fabricated by a one-step electrospinning technique. The diameters of the nanofibers range from 120 nm to 220 nm. The ERDN nanofibers, evenly distributed on the substrate with their random orientations, form a porous 3-D structure nanofibrous membrane. Compared to continuous thin films, the obtained nanofibrous membrane maintains a higher surface-area-to-volume ratio, a larger amount of immobilized-$Ru(bpy)_3^{2+}$, and a better stability of the $Ru(bpy)_3^{2+}$ immobilization. As a result, the nanofibers' ECL signal is enhanced ∼15-fold and stable (does not change during continuous CV scans for 50 cycles). As a sensing platform, the nanofibers can sensitively detect low concentration phenolic compounds by monitoring the phenol-dependent ECL intensity change. The detection limit for phenol is 1.0 nM based on a signal/noise ratio >3, which is comparable or better than that in reported phenol assays. In addition, the nanofibers exhibit excellent ECL behaviors on Au, Pt, GC and ITO electrodes. A great potential for ERDN nanofibers-based ECL sensors is offered.

Introduction

The immobilization of $Ru(bpy)_3^{2+}$ on an electrode surface has become a promising method and is widely used in electrochemiluminescence (ECL) sensors because it can create a supersensitive, cost-effective and regenerable sensing platform.[1–3] It is widely accepted that the following aspects' increase will contribute to an increase of the ECL sensor's sensitivity: (1) The surface area of the sensing platform; (2) The amount of immobilized $Ru(bpy)_3^{2+}$ on the electrode surface.[3–14] Much effort has been made to immobilize $Ru(bpy)_3^{2+}$ on electrode surfaces by different techniques, such as Langmuir-Blodgett films,[4] self-assembled monolayers,[5] layer-by-layer assembly,[6] covalent immobilization,[7,8] cation exchange polymers[9–11] and $Ru(bpy)_3^{2+}$-doped nanomaterials.[12–14] However, these approaches either are time-consuming or involve complicated fabrication processes. So it is still desired to develop a new, facile and inexpensive approach for fabricating ECL sensor interfaces that have high surface area and amount of immobilized $Ru(bpy)_3^{2+}$.

Recently, the electrospinning technique has been proven a simple, versatile and cost-effective approach for fabricating polymeric fibrous membranes with large surface areas.[15–20] These fibrous membranes show a great potential for sensors of high sensitivity.[17–20] Polydiacetylene-embedded silica-enforced fibers have been electrospun as a colorimetic sensor for volatile organic compounds.[17] Electrospun fluorescent polymer nanofibers have been designed and fabricated as a highly sensitive optical sensor for metal ions (Fe^{3+} and Hg^{2+}) and 2,4-dinitrotoluene. The Stern–Volmer constant (K_{SV}) values of these sensors are 2 to 3 orders of magnitude higher than those by thin film methods with the same

sensing material.[18] A fluorescence conjugated polymer has been synthesized and fabricated into electrospun fibers that can sense low concentration (ppb) cytochrome *c* and methyl viologen in aqueous solutions.[19] The electrospun light-emitting nanofibers have been fabricated from $[Ru(bpy)_3]^{2+}(PF_6^-)_2$/polyethylene oxide mixtures.[20] Deposited on gold interdigitated electrodes, and charged with operating voltages of 3 V or 4 V, the fibers show light emission in a dry nitrogen atmosphere.[20] But, to the best of our knowledge, the electrospinning technique has not been used in ECL sensors.

In this paper, we selected cation exchanger Nafion as the immobilization material for $Ru(bpy)_3^{2+}$ and fabricated electrospun $Ru(bpy)_3^{2+}$-doped Nafion (ERDN) nanofibers by electrospinning technique. As an interesting and useful ion-exchange material for $Ru(bpy)_3^{2+}$, Nafion has been widely used in electrochemistry.[11] Its ion-exchange selectivity coefficient (*vs.* Na^+) for $Ru(bpy)_3^{2+}$ is very large (5.7×10^6) because the sulfonic acid on it can strongly bind to $Ru(bpy)_3^{2+}$.[21] However, due to pure Nafion's intensive aggregates, its solution usually can only be electrosprayed into beads rather than be electrospun into nanofibers. On the other hand, the addition of polyelectrolytes can improve the polymer solution's properties (ionic strength, aggregation and viscosity, *etc.*), and therefore promote sufficient entanglement for proper electrospinning. The Nafion and Poly acrylic acid (PAA) blend solution can probably be electrospun to polyfibers.[22] In this paper, with only a little PAA, the complex-polymer ($Ru(bpy)_3^{2+}$/Nafion) solution was electrospun into ERDN nanofibers. By this method, the surface-area-to-volume ratio and immobilized $Ru(bpy)_3^{2+}$ of ERDN nanofibers might both be increased, therefore the ECL sensing platform based on ERDN nanofibers would probably show a strong ECL signal, and thus a high sensitivity in molecular detection (*e.g.* low-concentration phenolic compound). Compared to the common $Ru(bpy)_3^{2+}$ ECL system, this ERDN nanofibers exhibit several

College of Chemistry, Sichuan University, Chengdu, 610065, P. R. China. E-mail: xiaodan@scu.edu.cn; Fax: +86-28-85416029; Tel: +86-28-85415029

advantages such as facile fabrication, sensitive response and low consumption of expensive reagent. So a great potential for electrospun Nafion nanofibers-based ECL sensors is offered in this paper.

Experimental

Chemicals

Ru(bpy)$_3$Cl$_2$·6H$_2$O, tri-n-propylamine (TPrA, 98%), PAA (Mr = 450 000) and Nafion (5 wt%) were commercially purchased from Aldrich Co. Phenol, resorcin, hydroquinone and catechol were purchased from Chengdu Chemicals (Sichuan, China). All chemicals were of analytical grade and used without further purification. All solutions were prepared with doubly distilled water.

Instrumentation

Cyclic voltammetry (CV) and ECL signals were measured on a Reimai MIP-E ECL instrument (Xi'an, China). Electrochemical measurements were performed on a conventional three-electrode system. The bare or modified gold (Au), platinum (Pt), glassy carbon (GC) electrode and indium-doped tin oxide (ITO) electrodes were employed as the working electrodes, an Ag/AgCl (saturated KCl) as the reference electrode and a platinum wire as the counter electrode. The fluorescence spectrum and ECL emission spectrum were obtained on a fluorescence spectrophotometer (F-4500, Hitachi, Japan). The morphology of the nanofibers was investigated by scanning electron microscopy (SEM) (S-4800, Hitachi, Japan).

ECL and electrochemical characterization

The scan rate was 100 mV/s and the PMT high voltage was 800 V. All solutions were bubbled with a constant flow of N$_2$ before and during the measurements. All ECL measurements were conducted in a 5 mmol/L TPrA solution at 25 ± 1 °C. The pH of the phosphate buffer solution (PBS, 0.2 mol/L) was adjusted with concentrated NaOH or phosphoric acid. The reported ECL values were the average of at least three scans. The relative standard derivation was less than 3% (n = 3).

Electrospinning

A series of electrospinning solutions were prepared by mixing 5% m/m PAA in 3/1 isopropylalcohol/water with 5% m/m Nafion commercial solution at desired weight ratios. If added, the concentration of Ru(bpy)$_3$Cl$_2$·6H$_2$O was 1.0 mg/L. The electrospinning apparatus consisted of a high-voltage power supply (Series EL, Glassman High Voltage Inc.), a syringe pump, a syringe, a stainless steel needle (d = 0.55 mm) and a grounded collector (Aluminium foil or ITO fasted on the aluminium foil). The electrospinning solution was placed in the syringe. The needle was connected to the high-voltage supply which can generate positive voltage 50 kV. The spinning distance between the tip of the needle and the collector was about 23 cm. The positive voltage applied to polymer solutions was 15 kV. The flow rate of the solution was set at 0.8 ml/h by the syringe pump. All electrospinning experiments were carried out at room temperature. After the electrospun fibrous membrane was formed, it was gently striped from the aluminium sheet acceptor, placed over a beaker, and dried in an oven at 140 °C for 20 min.

Preparation of the working electrode

Clean Au (D = 2 mm), Pt (D = 5 mm), GC (D = 5 mm) and ITO (10 × 40 mm) electrodes were prepared according to reported methods, respectively.[23–25] Three different Ru(bpy)$_3^{2+}$-modified electrodes were prepared as following: (1) *The continuous thin film-modified Au electrode.* A clean Au electrode surface was coated with 1.0 μL electrospinning solution (containing Ru(bpy)$_3^{2+}$ (1.0 mg/ml), Nafion (71%) and PAA (29%)), and then dried at room temperature; (2) *The electrospun Ru(bpy)$_3^{2+}$-soaked nanofibers (ERSN)-modified Au electrodes.* The ERSN nanofibers were fabricated by electrospinning the solution above (without Ru(bpy)$_3^{2+}$) and its membrane was cut into a disk shape (diameter was the same as that of the Au electrode). The membrane was then tightly and smoothly put all over the surface of the Au electrode. Its edge was fixed by insulating pastern, and then dried at room temperature. The modified Au electrode was then immersed into a Ru(bpy)$_3^{2+}$ solution (4 × 10^{-5} M) for 40 min until the ECL signal was intensive and steady. After the immersion, the nanofibers are regarded to be saturated with Ru(bpy)$_3^{2+}$. (3) *The ERDN-modified electrodes.* The ERDN nanofibers were fabricated directly by electrospinning the same solution to (1), and then the ERDN nanofibers were modified on the Au electrode with the same processes as (2). By comparison, (3) were also applied to other electrodes (Pt and GC). The nanofibers-modified ITO electrode was fabricated by electrospinning the solution with the suitable volume on the ITO surface directly, since the ITO can be used as the nanofibers' collector during the electrospinning process.

Results and discussion

Fig. 1 represents the schematic procedure for one-step fabrication of ERDN nanofibers. Nafion has a fluorocarbon backbone with a sulfonic acid pendant group that binds strongly to Ru(bpy)$_3^{2+}$. In aqueous solutions, due to the interaction between the sulfonic acid pendant group and cations, Nafion exhibits an aggregate formation: those ionic groups aggregate and tightly packed regions are formed. As a result of low viscosity and entanglement absence, the Ru(bpy)$_3^{2+}$/Nafion solution can only be electrosprayed. The addition of polyelectrolyte PAA can
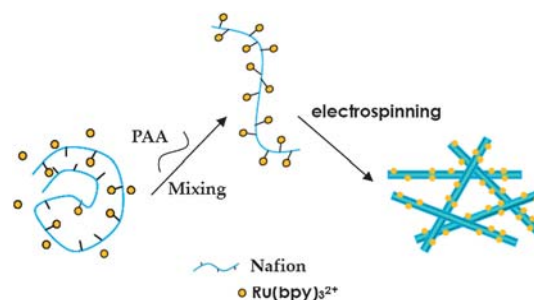
Fig. 1 Schematic illustration of the one-step process for fabricating ERDN nanofibers.
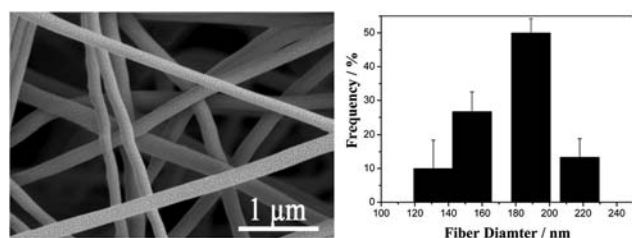
Fig. 2 SEM image (left) and the diameter distribution (right) of the ERDN nanofibers. The total polymer concentration of electrospinning solution is 5 wt% in 3/1 isopropyl alcohol/water. The Nafion content is 71%. The PAA content is 29%. The concentration of $Ru(bpy)_3^{2+}$ is 1.0 mg/ml.

strengthen the nafion's ionic environment and screen the electrostatic interactions of its ionic clusters, therefore a more extended formation results and more entanglements of the polymer Nafion chains. Consequently, the ERDN nanofibers are able to be fabricated by electrospinning technique.

Fig. 2 shows the SEM image of the porous electrospun Nafion nanofibrous membrane. It can be observed that the membrane has a 3-D structure. The ERDN nanofibers are evenly distributed on the substrate, and their orientations are random. The diameters of the nanofibers range from 120 nm to 220 nm. More uniform diameter fibers may be achieved by changing the conditions of the electrospinning process (the spinning distance, the concentration of the solution *et al.*). There are some merits from the nanometer scale: (1) The amount of immobilized-$Ru(bpy)_3^{2+}$ is significantly increased because when the Nafion aggregation is suppressed, the sulfonic acid groups inside Nafion are exposed to bind with $Ru(bpy)_3^{2+}$; (2) The surface-area-to-volume ratio of ERDN nanofibers is greatly increased, which promotes the efficient interactions between $Ru(bpy)_3^{2+}$ and TPrA; (3) Last but not least, the $Ru(bpy)_3^{2+}$ molecule can be uniformly, stably and efficiently immobilized into the Nafion nanofibers, which is a prerequisite for the realization of regenerable chemical sensors.

In order to demonstrate the advantage of the ERDN nanofibers in ECL amplification, we compared the different ECL behaviors between a thin film, ERSN nanofibers and ERDN
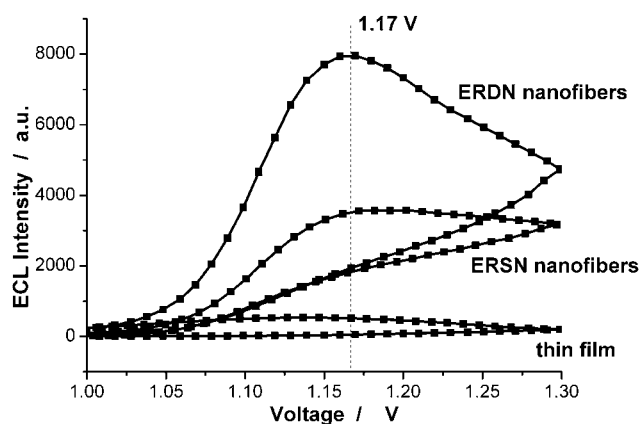
nanofibers on Au electrode (for fabrication details, see the experimental section), respectively. As shown in Fig. 3, in a 5 mM TPrA solution, the thin film shows a weak ECL signal beginning at ~0.7 V, peaking at ~1.2 V with an ECL intensity of 540 (a. u.). The ERSN nanofibers produce a high ECL signal in the same potential range. The ECL peak (3564 (a. u.)) is also near 1.2 V. Its intensity is 6.6 times higher than that of the thin film. The high ECL intensity might be ascribed to the efficient interactions between $Ru(bpy)_3^{2+}$ and TPrA due to the porosity and the high surface-area-to-volume ratio of the ERSN nanofibrous membrane. For ERDN nanofibers, the intensity of the ECL peak (near 1.2 V) is significantly enhanced, 14.7 times and 2.2 times higher than that of the thin film and the ERSN nanofibers, respectively. Since the thin film and the ERDN nanofibers are both fabricated with the same electrospinning solution, such enhanced ECL intensity of the ERDN nanofibers might be attributed to the greatly increased surface-area-to-volume ratio, and more importantly, the more uniform, stable and efficient immobilization of $Ru(bpy)_3^{2+}$. In addition, the ECL intensity of ERDN nanofibers is 2.2 times higher than that of ERSN nanofibers. A cause for the intensity enhancement can be the increased amount of immobilized-$Ru(bpy)_3^{2+}$ on the former nanofibers, which results from the larger specific surface of the former nanofibers for $Ru(bpy)_3^{2+}$. The different ECL signals of ERDN-modified electrode with and without immersing into $Ru(bpy)_3^{2+}$ solution (4.0×10^{-6} M) were also compared. The bare electrode in the $Ru(bpy)_3^{2+}$ solution exhibited the same ECL intensity as the ERDN-modified electrode in the absence of $Ru(bpy)_3^{2+}$. However, the ECL signals of the ERDN-modified electrode in the $Ru(bpy)_3^{2+}$ solution almost remained steady within the first 10 min, and then slowly increased until a plateau (the relative ECL intensity is 145%) was reached after 30 min. These results indicated that the electron transfer on the ERDN nanofibers was much more efficient than that in the $Ru(bpy)_3^{2+}$ solution.

Since the ERDN nanofibers showed advantage in ECL amplification on Au electrodes, their good ECL behaviors on different electrodes may provide a general sensing method for molecular detection. Fig. 4 shows the ECL processes and CVs of the ERDN nanofibers on Au, Pt, GC and ITO electrodes (in a low concentration TPrA solution (5 mM, pH = 7.5)). (1) *The nanofibers-modified Au electrode.* The anodic current increases at 0.7 V (corresponding to direct oxidation of TPrA), drops after 0.9 V and increases again beyond 1.0 V (upon the oxidation of $Ru(bpy)_3^{2+}$). Meanwhile, the ECL intensity increases sharply and the ECL peak appears at 1.17 V. (2) *The nanofibers-modified Pt electrode.* When the electrode potential is scanned positively beyond 0.9 V (upon the oxidation of $Ru(bpy)_3^{2+}$), the ECL signal increases rapidly and peaks at about 1.18 V. (3) *The nanofibers-modified GC electrode.* A strong ECL signal with an intensity of 12000 (a. u.) is observed at about 1.25 V. (4) *The nanofibers-modified ITO electrode.* A high ECL intensity (3500 (a. u.)) is observed at about 1.25 V. In summary, the ERDN nanofibers show excellent ECL behaviors though different ECL intensities are observed on Au, Pt, GCE and ITO electrodes. This would facilitate a wide application of the ERDN nanofibers-based ECL sensor to environment detection.

To characterize the ERDN nanofibers, the well-known $Ru(bpy)_3^{2+}$/TPrA ECL system was used in this paper. Generally, in the ECL process, the strongly reducing intermediate TPrA·

Fig. 3 ECL amplification of the ERDN nanofibers in 5 mM TPrA solution (pH = 7.5).
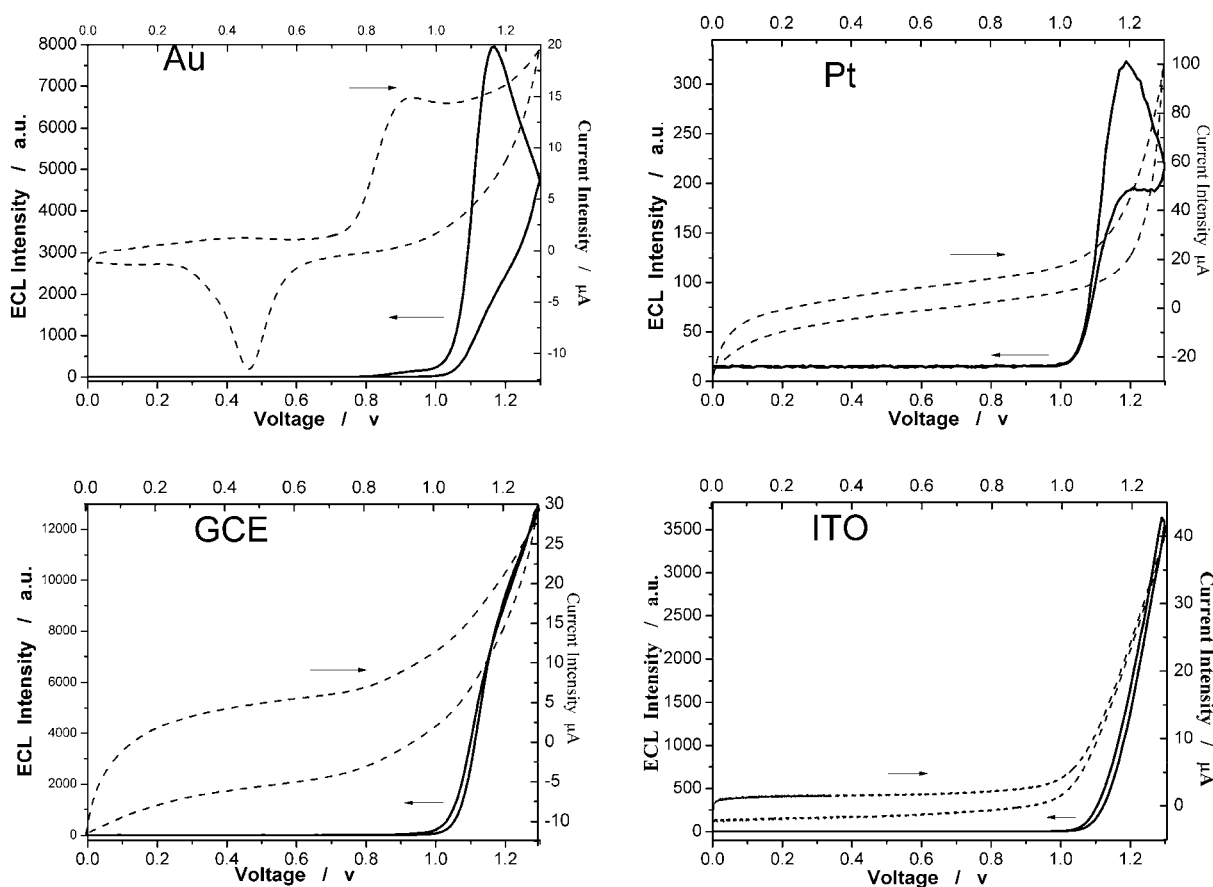
Fig. 4 ECL behaviors (solid line) and CVs (dot line) of ERDN nanofibers modified on Au, Pt, GCE and ITO electrodes in 5 mM TPrA solution (pH = 7.5).

reduces the electrogenerated $Ru(bpy)_3^{3+}$ to the Metal-to-Ligand Charge-Transfer (MLCT) excited state $Ru(bpy)_3^{2+*}$ that emits light. Fig. 5A shows the ECL intensity-potential curve of the electrospun nanofibers-modified Au electrode (in 0.2 M PBS solution (pH = 7.5) containing 5 mM TPrA). The ECL signal increases sharply at 0.9 V and reaches its peak at 1.17 V. The potential corresponding to the ECL peak of nanofibers is close to that in the $Ru(bpy)_3^{2+}$ solution system under the same experimental conditions.[19] The ECL emission spectrum of the electrospun nanofibers is also recorded at the scan potential of 1.30 V on the surface of an ITO electrode. Fig. 5B shows that the maximum emission wavelength of the ECL spectrum is at ∼ 610 nm. The result is identical to that of the previous report about the $Ru(bpy)_3^{2+}$ solution system.[23] It indicates that the emitter of the electrospun $Ru(bpy)_3^{2+}$-doped nanofibers is still $Ru(bpy)_3^{2+*}$. The ECL intensity of the electrospun nanofibers almost do not change during continuous CV scans for 50 cycles (inset of Fig. 5b) and do not decrease after 30 days of storage at room temperature, which indicates that the ECL signal of the electrospun nanofibers has a good stability.

Since in this paper cation exchanger Nafion is used as the immobilization material for $Ru(bpy)_3^{2+}$ and the basic material for fabricating ERDN nanofibers, an optimum Nafion content in the nanofibers is very important to achieve a strong and stable ECL signal. A series of blend solutions with different Nafion/PAA weight ratios were used as electrospinning solutions.

The concentration of $Ru(bpy)_3^{2+}$ in all above solutions was kept at 1.0 mg/ml. When the Nafion/PAA weight ratio was 1 : 1 or lower, smooth electrospun fibers could be obtained but dissolved into amorphism quickly in air. When the ratio was up to 3.5 : 1, stable electrospinning could not be observed because the polymer jet was occasionally blocked. After optimization, electrospun Nafion nanofibers fabricated at the ratio of 2.5 : 1 showed a high and stable ECL signal. $Ru(bpy)_3^{2+}$ ECL is always sensitive to pH value. In this paper, we studied the effects of different pH values (from 4.5 to 9.5) on the ERDN nanofibers' ECL intensity. As shown in Fig. 6, the maximum ECL emission of electrospun nanofibers is observed when the pH is 7.5. The ECL signal of the nanofiber decreases dramatically when the pH is either higher or lower than 7.5, and almost disappears in highly alkaline conditions (higher than pH 9.5).

Phenolic compounds are pharmaceutically and environmentally important compounds. It has been reported that phenolic compounds exhibit a quenching effect on $Ru(bpy)_3^{2+}$ ECL signals due to the energy transfer from the excited state $Ru(bpy)_3^{2+*}$ to the electro-oxidation species of phenolic compounds.[26–28] A titration of phenol was carried out to determine the sensitivity of ERDN nanofibers-based ECL sensors. The titration curve (Fig. 7) showed a monotonic decrease of the ECL intensity with the increase of phenol until complete quenching was reached in the presence of 2.0×10^{-4} M phenol. There was a good linear relation between the ECL decrease and

A

B
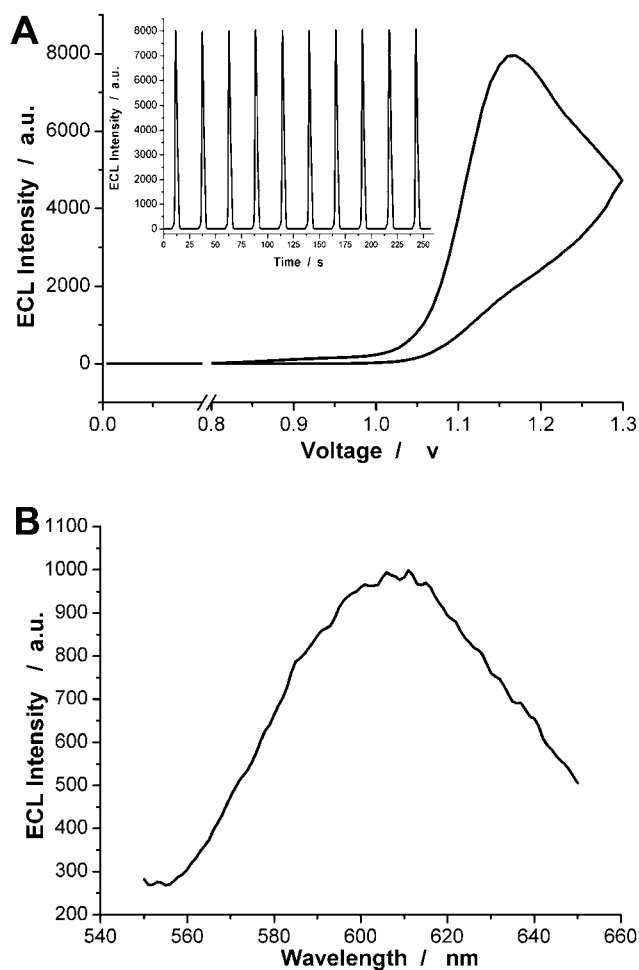
Fig. 5 Characterization of the ERDN nanofibers in 5 mM TPrA solution (pH = 7.5). A. ECL behavior of an ERDN nanofibers-modified gold electrode. Inset of figure 5A. Corresponding ECL intensity–time curve under continuous CV scans for 50 cycles. B. ECL emission spectrum of an ERDN nanofibers-modified ITO electrode.
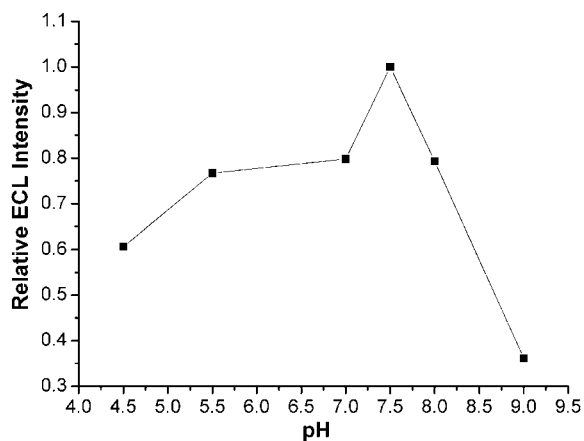
Fig. 6 Effect of pH on ECL signals of ERDN nanofibers in 5 mM TPrA solution.

the phenol concentration from 0 to 10 μM with a relative coefficient of 0.995. The detection limit for phenol was experimentally determined to be 1.0 nM based on a signal/noise ratio of >3.
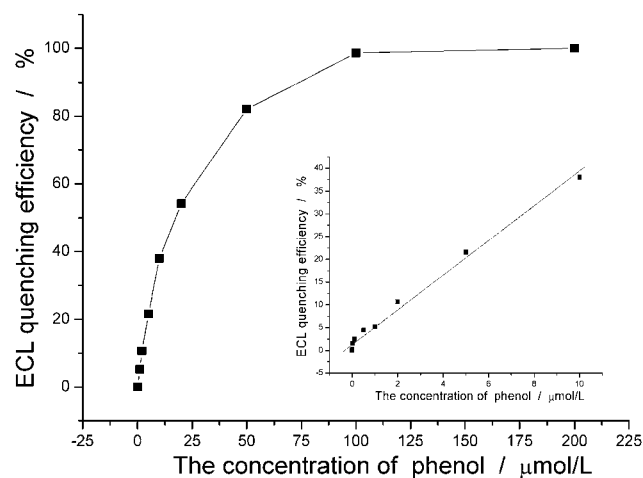
Fig. 7 Titration of phenol in the concentration range of 0–200 μM and 0–10 μM (*inset*). The *dots* are average experimental data from three parallel experiments and the *line* is the fitting curve. The ERDN nanofibers-modified gold electrode was used as the working electrode.

The detection limit is comparable or better than that in reported phenol assays.[29–32] The method is very simple because there is no need for pretreatment including preconcentration and solvent extraction. Phenol quenching efficiencies on ECL signals from ERDN nanofibers and from the $Ru(bpy)_3^{2+}$ solution system were also compared. The definition of the quenching efficiency is $(I_0 - I)/I_0$, where I and I_0 represent the ECL intensity with and without the quencher, respectively. For the $Ru(bpy)_3^{2+}$ solution ECL system, the quenching efficiency is about 36%[26,27] when the concentration of phenol is 2.0×10^{-5} M. However, using ERDN nanofibers as the sensing platform, 2.0×10^{-5} M phenol results in a high quenching efficiency of 54.2% ± 2.8%. The quenching efficiency for the ERDN nanofibers–based sensor attains 1.6 times higher than that in the $Ru(bpy)_3^{2+}$ solution ECL system. Additionally, complete quenching is observed in the presence of 2.0×10^{-4} M phenol for the ERDN nanofibers. However, in the $Ru(bpy)_3^{2+}$ solution ECL system, 1.0×10^{-3} M phenol results in only 95% but not complete quenching.[28] Furthermore, different quenching efficiencies between phenol, catechol, hydroquinone and resorcin were also observed (Table 1). Phenol and resorcin show high quenching efficiencies. With a concentration of 2.0×10^{-5} M, they display quenching efficiencies of 54.2% ± 2.8% and 61.4% ± 5.8%, respectively. Although catechol and hydroquinone can hardly match the quenching efficiencies above at the same concentration, they also exhibit efficiently quenching efficiencies of 87.6% ± 1.1% and 82.1% ± 1.5% with

Table 1 The quenching effects of phenolic compounds on ECL signals of the ERDN nanofibers. The concentration of TPrA is 5 mM (pH = 7.5). The potential is 1.17 V

Compound	Phenol[a]	Resorcin[a]	Catechol[b]	Hydroquinone[b]
$(I_0 - I)/I_0$ (%)	54.2% ± 2.8%	61.4% ± 5.8%	87.6% ± 1.1%	82.1% ± 1.5%

[a] The concentration of the compound is 2.0×10^{-5} M. [b] The concentration of the compound is 2.0×10^{-4} M.

a concentration of 2.0×10^{-4} M, respectively. This offers great potential for detecting phenolic compounds using ERDN nanofibers-based ECL sensors.

Conclusion

In this paper, a new, simple and general ECL sensing strategy for analytical applications is provided. With Nafion as the immobilization material, ERDN nanofibers were fabricated by one-step electrospinning technique. Compared to continuous thin films, the ERDN nanofibers had an enhanced (~15-fold) and stable ECL signal. The ERDN nanofibers also exhibited excellent ECL behaviors on Au, Pt, GC and ITO electrodes. A high quenching efficiency on the ECL signal was obtained with the presence of low concentration phenolic compounds. The detection limit for phenol was experimentally determined to be 1.0 nM based on a signal/noise ratio of >3. The detection limit is comparable or better than that in reported phenol assays. Indeed, as a sensing platform, the electrospun nanofibers have merits including increased amount of immobilized-$Ru(bpy)_3^{2+}$ and high surface-area-to-volume ratio. All above results demonstrate that electrospun nanofibers-based ECL sensors have a great potential for routine analyses.

Acknowledgements

References

1 Z. F. Ding, B. M. Quinn, S. K. Haram, L. E. Pell, B. A. Korgel and A. J. Bard, *Science*, 2002, **296**, 1293.
2 W. J. Miao, *Chem. Rev.*, 2008, **108**, 2506.
3 M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003.
4 C. H. Lyons, E. D. Abbas, J. K. Lee and M. F. Rubner, *J. Am. Chem. Soc.*, 1998, **120**, 12100.
5 C. J. Miller, P. McCord and A. J. Bard, *Langmuir*, 1991, **7**, 2781.
6 Z. H. Guo, Y. Shen, M. K. Wang, F. Zhao and S. J. Dong, *J. Am. Chem. Soc*, 2004, **76**, 184.
7 S. Zanarini, E. Rampazzo, L. D. Ciana, M. Marcaccio, E. Marzocchi, M. Montalti, F. Paolucci and L. Prodi, *J. Am. Chem. Soc.*, 2009, **131**, 2260.
8 X. B. Yin, S. J. Dong and E. K. Wang, *TrAC, Trends Anal. Chem.*, 2004, **23**, 432.
9 H. N. Choi, S. Cho and W. Lee, *Anal. Chem.*, 2003, **75**, 4250.
10 Z. H. Guo and S. J. Dong, *Anal. Chem.*, 2004, **76**, 2683.
11 D. J. Kim, Y. K. Lyu, H. N. Choi, I. H. Min and W. Y. Lee, *Chem. Commun.*, 2005, **23**, 2966.
12 L. H. Zhang, Z. A. Xu, X. P. Sun and S. J. Dong, *Biosens. Bioelectron.*, 2007, **22**, 1097.
13 L. H. Zhang and S. J. Dong, *J. Anal. Chem. Soc*, 2006, **78**, 5119.
14 X. P. Sun, Y. Du, L. X. Zhang, S. J. Dong and E. K. Wang, *Anal. Chem.*, 2007, **79**, 2588.
15 F. D. Benedetto, A. Camposeo, S. Pagliara, E. Mele, L. Persano, R. Stabile, R. Clingolani and D. Pisignano, *Nat. Nanotechnol.*, 2008, **3**, 614.
16 D. Y. Yang, B. Lu, Y. Zhao and X. Y. Jiang, *Adv. Mater.*, 2007, **19**, 3702.
17 J. Yoon, S. K. Chae and J. M. Kim, *J. Am. Chem. Soc.*, 2007, **129**, 3038.
18 X. Y. Wang, C. Drew, S. H. Lee, K. J. Senecal, J. Kumar and L. A. Samuelson, *Nano Lett.*, 2002, **2**, 1273.
19 X. Y. Wang, Y. G. Kim, C. Drew, B. C. Ku, J. Kumar and L. A. Samuelson, *Nano Lett.*, 2004, **4**, 331.
20 J. M. Moran-Mirabal, J. D. Slinker, J. A. DeFranco, S. S. Verbridge, R. Llic, S. Flores-Torres, H. Abruna, G. G. Malliaras and H. G. Craighead, *Nano Lett.*, 2007, **7**, 458.
21 M. N. Szentirmay and C. R. Martin, *Anal. Chem.*, 1984, **56**, 1898.
22 H. Chen, J. D. Snyder and Y. A. Elabd, *Macromolecules*, 2008, **41**, 128.
23 Y. B. Zu and A. J. Bard, *Anal. Chem.*, 2000, **72**, 3223.
24 C. Malins, R. Vandeloise, D. Walton and E. V. Donckt, *J. Phys. Chem. A*, 1997, **101**, 5063.
25 Z. F. Chen and Y. B. Zu, *Langmuir*, 2007, **23**, 11387.
26 H. Cui, F. Li, M. J. Shi, Y. Q. Pang and X. Q. Lin, *Electroanalysis*, 2005, **17**, 589.
27 H. Z. Zheng and Y. B. Zu, *J. Phys. Chem. B*, 2005, **109**, 16047.
28 J. McCall, C. Alexander and M. M. Richter, *Anal. Chem.*, 1999, **7**, 2523.
29 K. S. Khachatryan, S. V. Smirnova, I. I. Torocheshnikova, N. V. Shvedene, A. A. Formanovsky and I. V. Pletnev, *Anal. Bioanal. Chem.*, 2005, **381**, 464.
30 Z. L. Zhi, A. Ríos and M. Valcárel, *Analyst*, 1996, **121**, 1.
31 F. L. Qiu and R. G. Compton, *Analyst*, 2000, **125**, 531.
32 G. L. Chen, S. Y. Suen, S. Vied, K. Pickering, C. Perrin and E. D. Conte, *Analyst*, 2009, **134**, 331.