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Development of a reagentless electrochemiluminescent electrode for flow injection analysis using copolymerised luminol/aniline on nano-TiO_2 functionalised indium-tin oxide glass

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ABSTRACT

In this study, a nano-structured copolymer of luminol/aniline (PLA) was deposited onto nano-TiO_2-functionalised indium tin oxide (ITO)-coated glass by electrochemical polymerisation using cyclic voltammetry (CV). The resulting reagentless electrochemiluminescent (ECL) electrode (ECLode) can be used for flow injection analysis (FIA). The properties of the ECLode were characterised by CV, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The ECLode has high background ECL emission as well as excellent stability and reproducibility, and yielding sensitive response towards target analytes. The ECL emissions of the ECLode were 50 times higher than PLA/ITO, and 500 times higher than polyluminol (PL)/ITO. The ECLode showed sensitive responses to reactive oxygen species (ROSs), permitting its application for determination of antioxidants by quenching. Under optimised conditions, an absolute detection limit of 69.9 pg was obtained for resveratrol, comparable to the highest levels of sensitivity achieved by other methods. Thus, the gross antioxidant content of red wine was determined, with satisfactory recoveries between 87.6% and 108.3%. These results suggest a bright future for the use of the ECLode for single-channel FIA due to its high sensitivity, accuracy and reproducibility.

1. Introduction

Electrochemiluminescence (ECL) is an electronically induced physicochemical process by which luminescent excitons are generated on electrode surfaces, undergoing electron transfer reactions and emitting light during the de-excitation process [1]. ECL has been widely applied in immunoassays, clinical diagnosis and trace detection due to its high sensitivity, low background signal and wide dynamic range, as well as the simple instrumentation used [2–4]. One of the most important reagents used in ECL is luminol as in chemiluminescence (CL) analysis [5,6]. Flow injection analysis (FIA) is a promising application of ECL analysis [7]. The mixing of luminescent reagents with detection targets is an indispensable part of FIA, imposing strict requirements on instruments in order to achieve a reproducible signal. The longitudinal diffusion of target components in a complex pipe-line-based system during mixing may result in a decrease in sensitivity as well as accuracy. Rather than controlling a multi-channel system with sophisticated instruments [8], it is more effective to use a single-channel system [9] to overcome these problems. Development of a reagentless system may be one of the most promising strategies to avoid the conventional introduction of luminescent reagents [10,11]. Thus, the immobilisation of luminol on the electrode surface may permit simplification of FIA devices.

The electro-polymerisation of luminol has been carried out to immobilise it on the surface of glassy carbon [12–15], gold [13–16] or Pt [17] electrodes. Our group has studied the electro-polymerisation of luminol in order to immobilise it on the surface of indium tin oxide (ITO) glass [18]. In previous reports, cyclic voltammetry was used to polymerise luminol [12–17]. However, the unitary polyluminol (PL)-modified electrode was not optimal due to its poor electroactivity and low luminous emissions and stability [18,19]. In recent years, doped polymers have been adopted to improve the properties of modified electrodes. Wang immobilised luminol with cobalt at the electrode surface, and applied it in the detection of glucose [20]. Li prepared poly (luminol/aniline) (PLA) composite nanowires to modify a graphite electrode and investigated its ECL response to H_2O_2 and glucose [19]. Polyaniline (PANI), one of the most important conductive polymers, has attracted much attention due to its desirable electrical, electrochemical and optical properties, as well as its excellent environmental stability [21,22].

Because aniline is a substructure of luminol, the copolymerisation of luminol with aniline is feasible using the same approaches as used for the polymerisation of the individual compounds [15,17]. The copolymer is produced via the linkage of para-position

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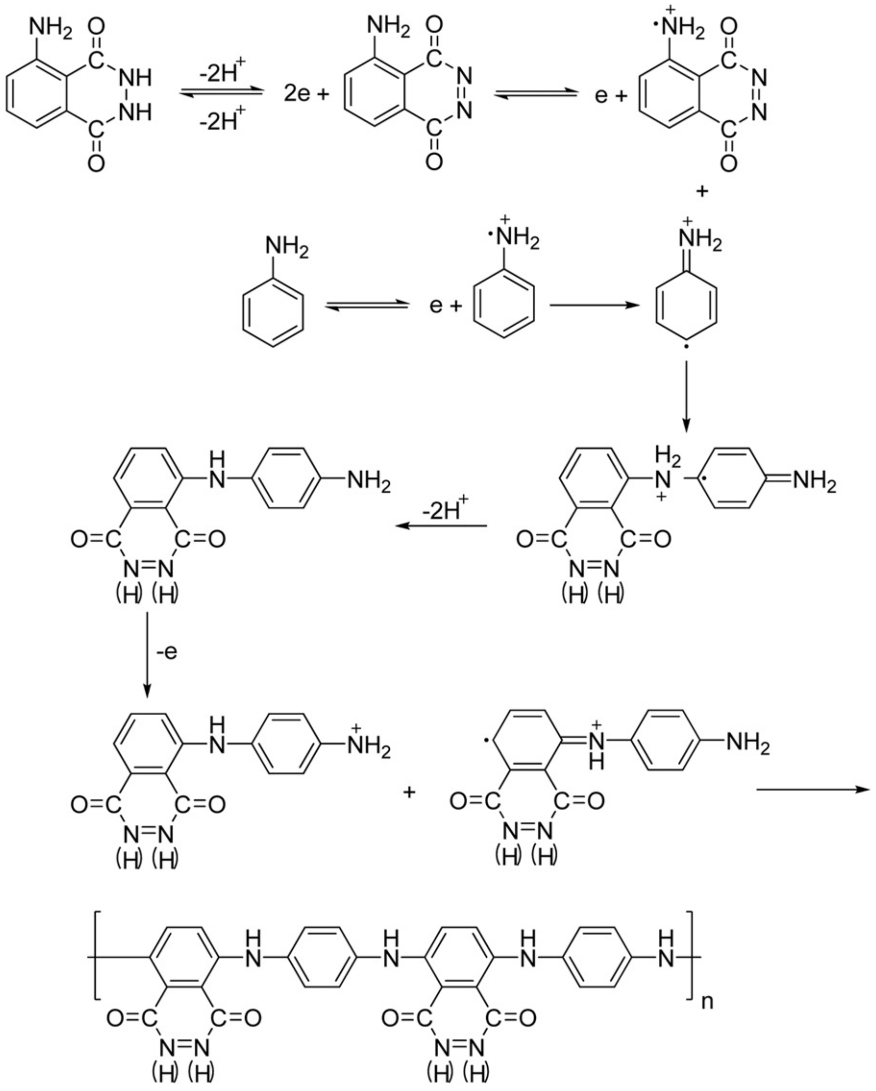


Scheme 1. The process of copolymerisation of luminol/aniline.

amidogen and two phenyl rings (as illustrated in Scheme 1). The aniline molecules introduced between luminol molecules form a linear chain of PANI, which promotes charge transfer within the copolymer. In this copolymer, the hydrazide group – the luminous moiety of luminol – retains electrochemical activity, inducing ECL emissions.

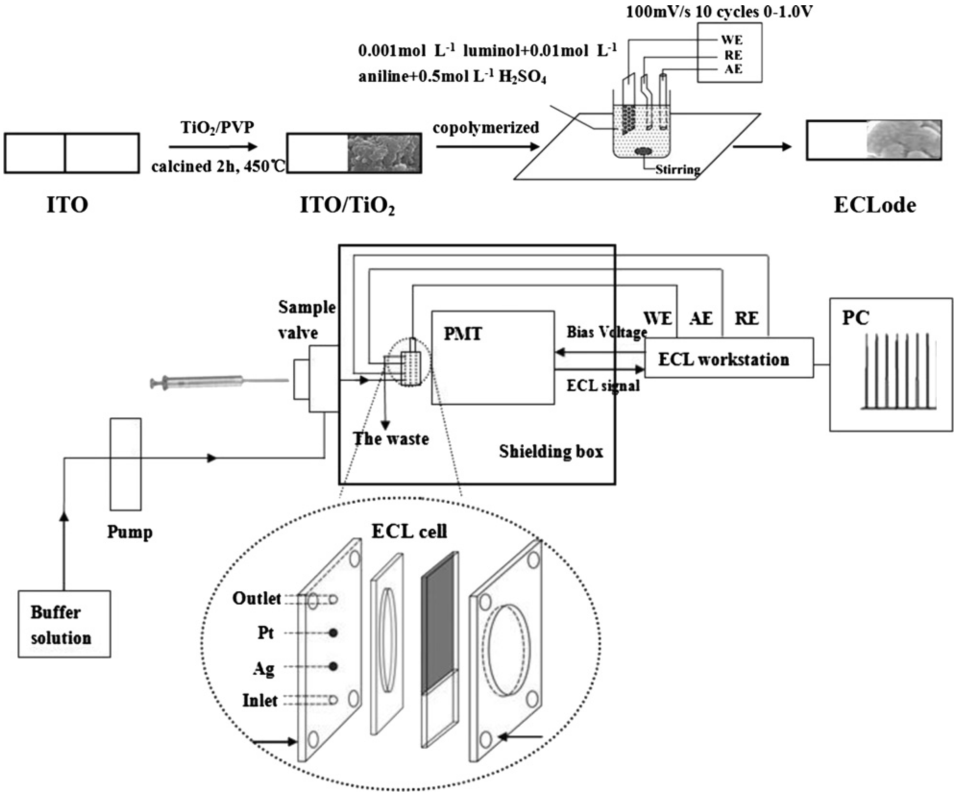
In our previous studies [23–25], nano-materials such as nano-metals and nano-metal oxides (especially nano-TiO_2) enhanced the ECL efficiency of luminol. Titanium dioxide (TiO_2), especially nano-TiO_2, has been widely used as a photocatalyst for the degradation of organic contaminants and as a photoanode for solar cells due to its high photochemical activity, semi-conductivity, insertion host capacity, and its low toxicity and cost [26]. Being highly ordered, TiO_2 possesses great surface area, and can provide a large number of active sites for adsorption or chemical/electrochemical reactions [27]. Moreover, it possesses not only favourable charge-transport properties [28] but also good biocompatibility [29]. Hence, some researchers have focused on the modification of electrode surfaces with nano-TiO_2 and presented mechanisms for its ECL-enhancing effect [25–27]. In previous research, we focused on the enhancement of luminol's ECL using nano-TiO_2. We concluded that the abundant electron/hole (e^-/h^+) couples in the outer shell of nano-TiO_2 could create more excitons of luminol and enhance its ECL via interaction with adsorbed luminol, coupled with the effects of reactive oxygen species (ROSs) [30].

In this paper, we report the preparation of a reagentless ECL electrode (ECLode) with PLA as luminophore on nano-TiO_2 functionalised ITO glass by means of cyclic voltammetry (CV); the resulting ECLode is suitable for use in FIA. The use of PLA greatly improves the performance of the ECLode in FIA. The nano-TiO_2 matrix gives higher surface loading of the polymer and improved catalysis in ECL. As result, this ECLode gave sensitive responses to antioxidants and was successfully applied in their determination. The gross antioxidant content of red wine was determined using this ECL-FIA technique, expressed as an equivalent amount of resveratrol. The results suggest great potential for further applications of this ECLode.

2. Experiments

2.1. Materials

Luminol was purchased from Fluka (USA). Nano-TiO_2 was obtained from Nanjing High Technology Nano Material Co. Ltd. (Nanjing, China). Resveratrol (HPLC >98%), polyvinylpyrrolidone



Scheme 2. The flow chart of PLA/nano-TiO_2 ECLode preparation and the installation of improved ECL-FIA device.

(PVP, k-30), aniline and other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were of analytical grade and were used without further purification. Ultrapure water (prepared by an ALH-6000-U ultrapure water machine, Aquapro, China) was used in all experiments.

2.2. Apparatus

ITO glass was purchased from Suzhou Nippon Sheet Glass Electronics Co. Ltd. (Suzhou, China). A lab-built ECL-FIA system [31] was used that required only one channel (see Scheme 2). It contained a flow ECL cell (approximately 5 μL inner volume) and a six-way sample injector with a 5 μL injection loop. An RST-600 Electrochemical Workstation (custom-built, Risetest Instrument Co. Ltd., Suzhou, PR China) was used to excite the ECL and record signals. An R212 photomultiplier tube (Hamamatsu, Japan) was used as an ECL detector (−800 V bias potential). All electrochemical investigations were performed on an RST-3000 Electrochemical Workstation (Risetest Instruments Co. Ltd. Suzhou, China). Scanning electron microscopy (SEM) was used to observe micromorphology (S-4700 scanning electron microanalyzer, Hitachi, Japan).

2.3. Preparation of PL, PLA and PLA/nano-TiO2 ECL electrodes

Pieces of ITO glass (1 cm×5 cm) were used as basal electrodes. Working area was not determined precisely because it was contingent on the size of the FIA-ECL cell. After sequential pretreatment in an ultrasonic bath with water, acetone, ethanol:1 mol L^{-1} NaOH (1:1, v/v) and water for 15 min each, and drying under a stream of nitrogen; the electrode was used as the working electrode in a normal three-electrode system to carry out electro-polymerisation in CV mode in stirred solution of 0.5 mol L^{-1} H_2SO_4 containing luminol (0.001 mol L^{-1}) or luminol and aniline (0.001 mol L^{-1} and 0.01 mol L^{-1}, respectively) within the range 0–1.0 V. The PLA/nano-TiO_2 ECLode was prepared similarly, but a dispersion of anatase nano-TiO_2/ PVP was first cast onto the ITO glass and sintered at 450 °C for 2 h (see Scheme 2).

2.4. Optimisation of the ECLode

In preparing the ECLode, we optimised parameters that strongly influenced ECL performance, such as scan rate and cycles of CV, temperature, stirring status, concentration of PVP and amount of nano-TiO_2. Detection conditions such as upper limiting potential, pulse period and pump flow rate also influenced the ECL performance and required optimisation.

2.5. Determination of gross antioxidant content in red wine

Based on background ECL emissions from this ECLode, the ECL-FIA platform was suitable for quantitative analysis of some trace constituents such as antioxidants, due to capture or neutralisation of free radicals, which quench the ECL. The gross antioxidant content of red wine could be determined, expressed as an equivalent amount of resveratrol. Following previously reported methods [32,33], tannin and ethanol were eliminated by antisolvent crystallisation (treated with saturated NaCl for 3 h, filtered) then boiled for 2 min. Finally, 5 μL of sample solution was injected into the FIA system after filtration through a 0.22 μm polypropylene membrane.

3. Results and discussion

3.1. Performance of the PLA modified layer

There have been few reports of PLA modified electrodes or descriptions of the mechanism of polymerisation [15,17]. As illustrated in Scheme 1, in an acidic medium, polymerisation between luminol and aniline would occur through the linkage of

–NH– with the para-carbon of the phenyl rings. The soft skeleton of the copolymer can form multiple structures by crinkling or folding. Here, a densely stacked porous structure was obtained, composed of spherical particles of approximately 30 nm diameter (see the SEM image, Fig. 1). After polymerisation, the luminophore of luminol (the hydrazide group –CO–NH–NH–CO–) was retained without structural alteration; thus, the copolymer retained its luminescence.

CV investigations indicate the contribution of aniline to the resulting polymer (Fig. 1C). As shown, luminol could be polymerised and deposited onto the electrode surface, but in very limited quantities and with low activity (curve a). Copolymerisation with aniline not only facilitated polymer growth but also promoted electrochemical activity (curve b). PLA gave a redox current at least 5 times higher than PL. The redox couple of approximately 0.46/0.57 V can be attributed to the superposition of the first redox step of luminol (0.50/0.60 V) and emeraldine/pernigraniline (0.42/0.48 V), while the new redox couple of approximately 0.17/0.21 V can be attributed to leucoemeraldine/emeraldine [34].

Electrochemical impedance spectroscopy (EIS) revealed the reasons for the improved performance of PLA, which was mostly due to the easier charge transfer that became possible when aniline units were inserted into the polymer. As shown in Fig. 1D, the PLA modified electrode (curve b) gave a smaller EIS signal than the PL modified electrode (curve c). In the Nyquist plots, the size of the semi-circle in the high frequency range reflects the charge transfer resistance (R_{ct}) of the modified layer. The deposition of PL on the electrode surface increased R_{ct}. However, R_{ct} was decreased by PLA, meaning that it had better conductivity. In either PL or PLA, the soft linear skeleton of PANI is the pivotal structure for electron transfer [34], but the more compact structure of PL due to its lateral hydrazide groups resulted in poor conductivity. In PLA, there were moderate intervals due to the insertion of aniline.

Because of the instability of aniline at high temperatures, room temperature is optimal (see Fig. 2A). The conditions for electropolymerisation must also be optimised. Fig. 2B,C shows the effect of scan rate (mV s^{-1}) and cycles on relative ECL intensity. Optimal sensitivity, repeatability and stability were achieved at 100 mV s^{-1} and 10 cycles. Higher scan rates or too many scans led to decreased ECL emissions. The poorer conductivity of the copolymer resulted from the lengthened chain and thicker film. EIS results suggest that R_{ct} increased with repeated CV cycles (Fig. 2D). Fig. 2C also indicates another important factor in the formation of PLA. Although it has a similar molecular structure in part, the molecular diffusivity of luminol is different than aniline's due to its different molecular weight and size. Stirring gave a copolymer with better uniformity and ECL performance than no stirring.

In our previous paper, we concluded that ECL intensity was affected by the performance of the FIA system [31] and by electric parameters. In this work, a buffer solution flow rate of 0.18 ml min^{-1} (see Fig. 2E) and an electric pulse of 2 s (see Fig. 2F) at a duty factor of 1:9 were optimal.

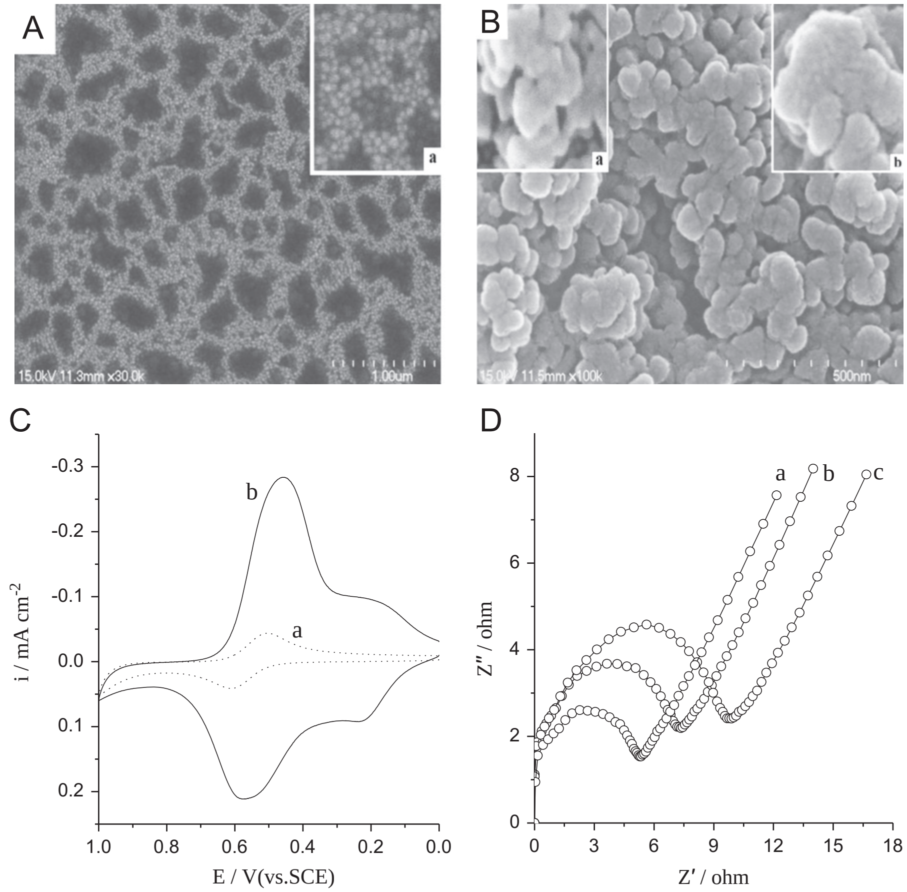


Fig. 1. The scanning electronic micrographs of (A) prepared PLA (here "a" is the partial enlarged detail); (B) prepared PLA on nano-TiO_2, and inset (a) is the morphology of nano-TiO_2 and inset (b) is the partial enlarged detail of PLA/nano-TiO_2; (C) The CV curves of (a) PL modified electrode and (b) PLA modified electrode in 0.5 mol L^{-1} H_2SO_4 within 0–1.0 V; and (D) The Nyquist plots of (a) bare ITO, (b) PLA-modified ITO and (c) PL modified ITO in 1 mol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$/1 mol L^{-1} NaCl solution within the frequency range from 1 Hz to 100 kHz.

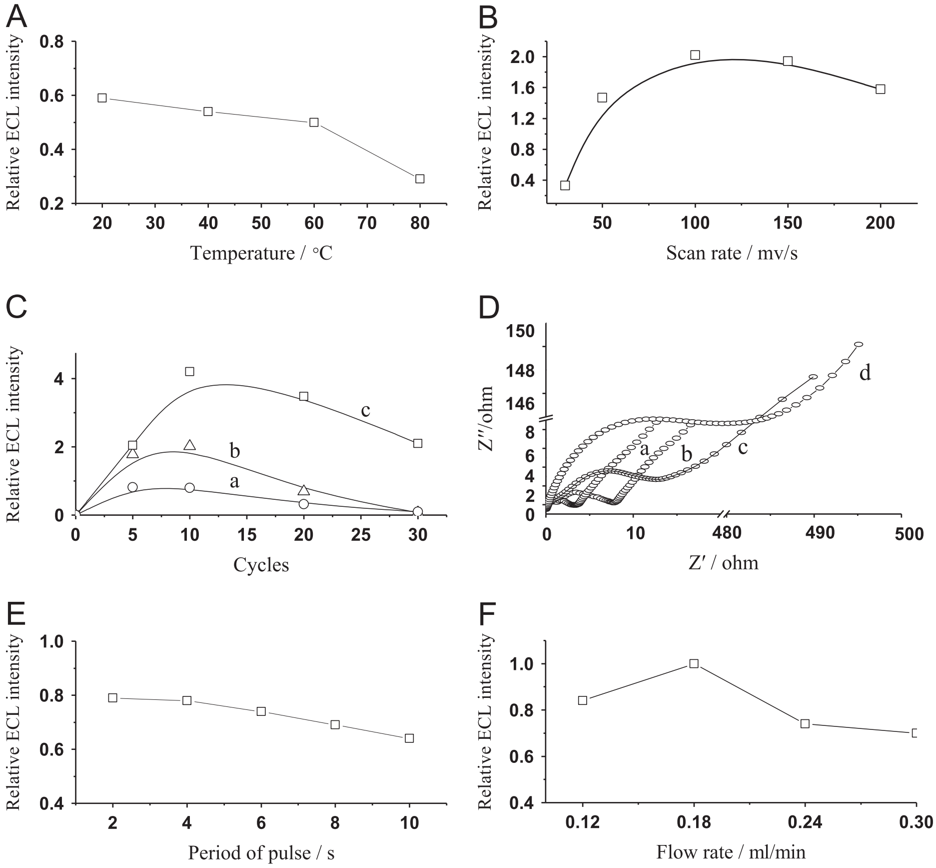


Fig. 2. The effect of (A) temperature, (B) scan rate and (C) cycles and stirring status on the ECL performance of prepared PLA modified electrode. In (C), there (a, b) are for PL or PLA without stirring and (c) is for PLA with stirring. (D) Displays the EIS responses upon different cycles (a: 10 cycles, b: 30 cycles, c: 100 cycles and d: 200 cycles). The effect of (E) the flow rate and (F) the pulse period on the ECL emission of PLA modified electrode during the FIA.

Applied pulse potential is another factor influencing ECL emission. It is not difficult to infer that the luminescence of PLA must be similar to luminol. Previous reports [18,35] indicate that, in alkaline solution, luminol is oxidised via a two-step process at a voltage of approximately 1.5 V, giving its excited state (3-aminophthalic acid dianion, the ring-opened intermediate form) and then emitting light at a wavelength of 425 nm during de-excitation. Luminol is consumed during ECL because this ring-opened oxidation is irreversible. However, our results suggest that in the presence of reactive oxygen species (ROSs) and nanomaterials, the intermediate produced in the first oxidation step may receive energy from ROSs, resulting in excitation and light emission [30,36], thus allowing detection without consumption of luminol. Fig. 3A shows the influence of the upper limiting potential on ECL emissions (at 0 V lower limiting potential). When the upper limiting potential was below 1.0 V, ECL intensity rose with increases in the applied voltage. However, when the applied potential exceeded 1.0 V, the luminophore in the copolymer was destroyed, resulting in an attenuated ECL signal. Thus, an upper limiting potential of 1.0 V was selected to ensure detection without consumption. This makes the use of a reagentless ECLode possible in FIA.

Under optimised conditions, Fig. 3B shows that the insertion of aniline in the polymer enhanced ECL intensity tremendously. Here, curve "a" is for the PL electrode, while curve "b" is for the PLA electrode. A ten-fold increased ECL signal was obtained using the PLA electrode. The PLA modified electrode also exhibited good stability and reproducibility. The relative standard deviation (RSD) for consecutive ECL pulses, repetitive detections and different electrodes were 1.4% ($n=7$), 3.0% ($n=7$) and 3.8% ($n=11$), respectively. Comparatively, the RSD for consecutive ECL pulses on PL electrode is 11.07% ($n=7$)

As previously discussed, reactive oxygen species such as H_2O_2 may enhance the ECL intensity of luminol or PL due to energy transfer to the oxidative intermediate of luminol. Under the abovementioned conditions in phosphate buffer (pH 10.0), the ECL intensity responded linearly to H_2O_2 concentration in the range of 1.0×10^{-6}–1.0×10^{-4} mol L^{-1}, with an absolute detection limit (LOD_m) of approximately 0.13 ng. This was lower than in a previous report [19].

3.2. ECL emissions of the PLA/nano-TiO_2 ECLode

As shown in Fig. 4A, the amount of nano-TiO_2 added strongly influenced the ECL emissions of the ECLode. ECL intensity increased with nano-TiO_2 quantity up to 2.5 mg. An excess of TiO_2 may reduce ECL transmission, and also give a less-compact film that is more likely to fall off. Thus, 2.5 mg was selected as the optimal amount. Used as a dispersant, PVP may prevent aggregation of nano-TiO_2 in aqueous solution, and also improve film formation. As shown in Fig. 4B, with increasing concentration of PVP, the ECL intensity first increased, and then it decreased. The critical concentration was 6 mg mL^{-1}. PVP is burned out during calcination in the muffle furnace. However, an excess may impair decomposition. Under these optimised conditions, the ECL intensity of the ECLode is shown as curve "c" in Fig. 3B, with 50 times higher ECL emission than from a PLA electrode. Additionally, the stability of this ECLode is very good (RSD=0.012%, $n=7$). The structure of the modified layer was characterised by SEM (Fig. 1B).

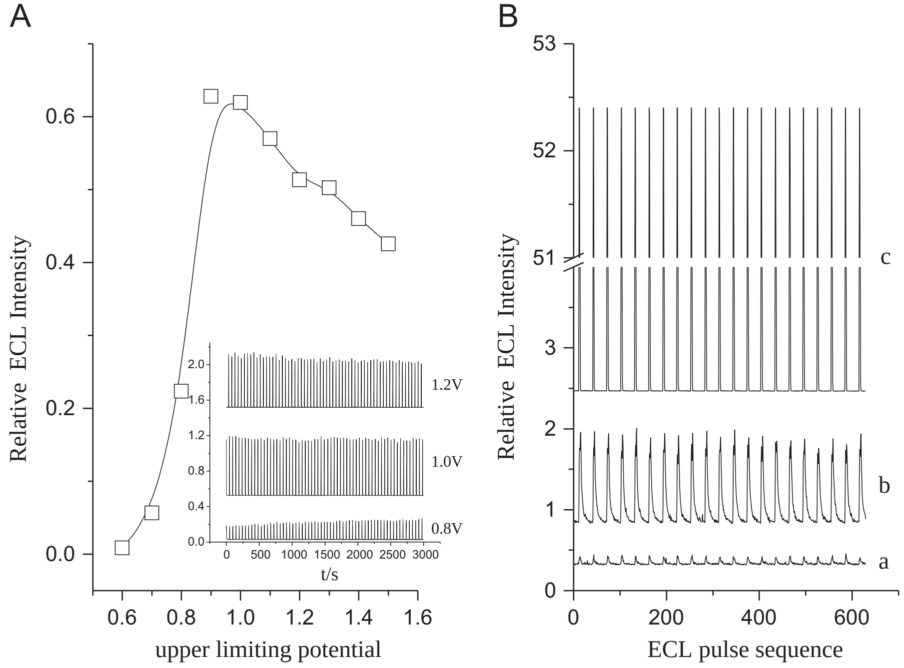


Fig. 3. (A) The effect of upper limiting potential on the ECL of resulted ECLode at the constantly 0 V of lower limiting potential (the inset is the figure of ECL signal at different upper limiting potential) and (B) the ECL signal on (a) PL/ITO, (b) PLA/ITO and (c) resulted PLA/nano-TiO_2 ECLode.

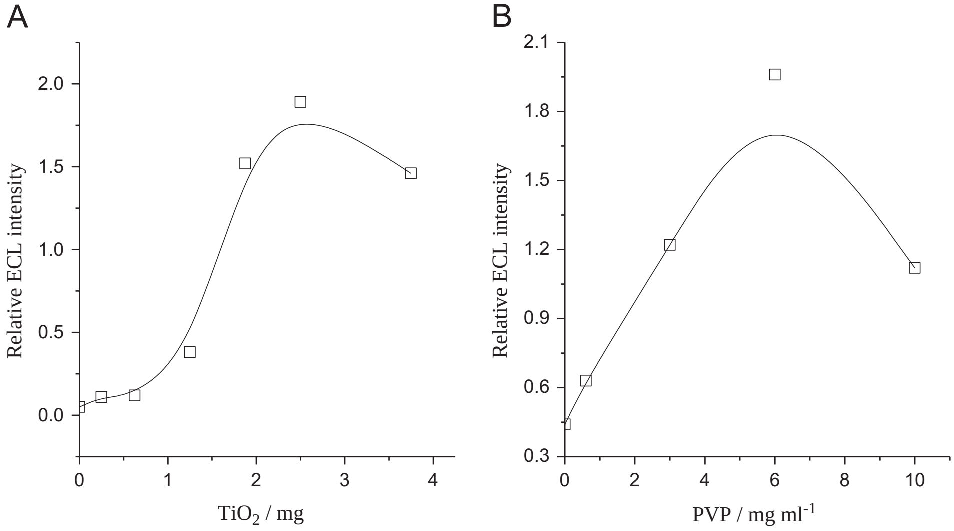


Fig. 4. The effect of (A) the dosage of nano-TiO_2 and (B) the content of PVP on performance of resulted PLA/nano-TiO_2 ECLode.

Particles of PLA are clearly visible on the surface of the nano-TiO_2 particles.

Nano-TiO_2 on ITO offers a moderate band gap (3.0–3.2 eV), as well as greater surface area and additional active sites to support PLA, which favours the generation of electron/hole couples (e^-/h^+) through the electron transition from the valence band to the conduction band. These couples, particularly the holes, may “snatch” the electrons from species on the surface, accelerating their oxidation. Thus, nano-TiO_2 catalyses the oxidation of the luminophore in PLA, enhancing its ECL [25,30].

3.3. Analysis of gross antioxidant capacity of red wine

As previously discussed [36], antioxidants may quench ECL. Thus, ECL electrodes may be applied to evaluate the efficiency of traces of antioxidants. The gross antioxidant content in red wine was determined by this ECL-FIA technique, expressed as an equivalent amount of resveratrol.

Under optimised conditions, the PLA/nano-TiO_2 ECLode could detect resveratrol with a linear response from 0.25 to 2.0 mg L^{-1} ($\Delta ECL=0.8692+105.8C_{resveratrol}$ (mg L^{-1}), $r=0.9987$). As seen in Table 1, the PLA/nano-TiO_2 ECLode has better linearity, higher sensitivity and a lower detection limit than the PLA ECLode. The LOD_m of 69.9 pg (S/N=3) was much lower than most other methods.

To assess the proposed ECL-FIA technique in the analysis of antioxidants in red wine, interference from major wine components such as organic acids, inorganic salts and saccharides was examined. The tolerance was set as the maximum concentration of the foreign species, which caused an approximately ±5% relative error in the determination. Foreign species were added to 1 mg L^{-1} resveratrol; their tolerable concentration ratios was over 100 for

Table 1
Analytical performance of the methods for resveratrol detection.

Method	Linear range (correlation coefficient)	LOD$_m$^{a}	Application/comments	Reference
FIA-CL	5.0×10^{-3}–2×10^{-1} mg L^{-1} (0.9997)	225 pg	Wine	[33]
ECL	0.05–12.6 mg L^{-1} (0.9969)	0.3 μg	Polygonum cuspidatum	[37]
CE-ED	0.5–100 mg L^{-1} (0.9993)	–	Wine, herb, cuspidatum, Zijin capsule	[38]
LC-fluorescence	0.040–0.242 mg L^{-1} (0.992)	360 pg	*Trans*-resveratrol in wine	[39]
FIA-fluorescence	3.3–100 ng mL^{-1} (–)	25 pg	Beer	[40]
HPLC-CL	0.5–750 μg L^{-1} (0.9978)	166 pg	*Trans*-resveratrol in wine	[41]
FIA-ECL	1.0–8.0 mg L^{-1} (0.9950)	3.2 ng	PLA/ITO electrode, wine	Current work
	0.25–2.0 mg L^{-1} (0.9987)	69.9 pg	PLA/nano-TiO$_2$/ITO electrode, wine	

[a] LOD$_m$: The absolute detection limit.

Table 2
Recovery of resveratrol for red wine sample.

Sample (mg L^{-1})	Added (mg L^{-1})	Found total (mg L^{-1})	Recovery (%)	RSD (%) (n=5)
2.95	1	3.84	89.3	2.15
	2	4.70	87.6	2.47
	3	5.77	94.0	1.86
	4	7.28	108.3	2.88

citric and tartaric acids, 500 for glucose, 10,000 for Na$^+$, K$^+$, Mg^{2+} and Cl$^-$ and 1000 for ethanol. The gross antioxidant content of red wine was equivalent to 2.95±0.21 mg L^{-1} resveratrol, which is consistent with previous reports [33,39].

Recovery tests were performed by the standard addition method. As shown in Table 2, different quantities of standard were added, and the total ECL intensity recorded. The calculated recoveries, ranging from 87.6% to 108.3%, demonstrate the satisfactory performance of this PLA/nano-TiO$_2$ ECLode.

4. Conclusion

Luminol, immobilised on nano-TiO$_2$-functionalised ITO by copolymerisation with aniline, yields a reagentless ECL electrode for use in FIA. After optimisation of copolymerisation and detection parameters, the ECLode showed excellent characteristics such as sensitivity and reproducibility. The ECLode gives 500 or 50 times higher ECL emissions than PL- or PLA-modified electrodes, clearly demonstrating the amplifying effect of nano-TiO$_2$. This ECLode has excellent sensitivity to antioxidants, with an absolute detection limit equivalent to 69.9 pg resveratrol. The practicality of the proposed ECLode has been validated by using it to determine the antioxidant content of red wine. There is a linear response to resveratrol concentration from 0.25 to 2 mg L^{-1}, and a recovery of 87.6–108.3%. The gross antioxidant content of red wine was equivalent to 2.95±0.21 mg L^{-1} resveratrol. This ECLode made reagentless FIA detection with a single-channel instrument possible, making ECL analysis more practicable. This creates a new methodology for highly sensitive and accurate FIA determination. With further miniaturisation of the ECL cell, it may even be possible to use this ECLode with a microfluidic system.

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