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Enhanced electrochemiluminescence by ZnO nanowires for taurine determination

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Abstract

A novel electrochemiluminescence (ECL) sensor for the sensitive detection of taurine was developed. Taurine contains an aliphatic amine that gives it co-reactant properties. The ECL response of the taurine/[Ru(bpy)₃]²⁺ system was analyzed on two different electrodes surfaces, screen-printed graphene and gold electrodes, before and after modification with ZnO nanowires (ZnO NWs). The ZnO NWs modified electrode yielded an enhanced ECL signal, allowing rapid detection of taurine at 5.5x10⁻⁶ mol L⁻¹ detection limit. The ECL signal is stable and reproducible. The sensor has been applied to the determination of taurine in a commercial taurine supplement.

Keywords: Taurine, Electrochemiluminescence, ZnO nanowires

1. Introduction

Taurine (2-amino ethanesulfonic acid) is a non-essential amino acid that is synthesized in the body from cysteine and methionine and it is the only known natural sulfonic acid. Taurine is a neurotransmitter and a small molecule that intervenes in the formation of bile and in many other functions and biological processes [1]. However, very little amount of taurine is synthesized in the human body, being this the most common cause of taurine deficiency. Hence, the use of taurine supplements is an interesting possibility in special cases. The effects of supplementing taurine during pregnancy have been studied and it has been found that it has a preventive role in reducing of alterations in pancreas programming that may be in turn related to the appearance of type 2 diabetes in the fetus [2]. Moreover, preliminary studies in male rats demonstrate that take taurine supplement may have a regulatory effect on the changes induced by diabetes in gonadal hormone levels, mainly testosterone [3]. Promising experimental results indicate the benefits of the supplementation of taurine together with anticonvulsant drugs to treat drug-resistant epilepsy [4]. Taurine should be also seriously reconsidered as a potential treatment for diseases related to the retina. Since they have studied that taurine may be related to the onset of glaucoma or diabetic retinopathy [5].

Therefore, the detection of taurine is of great importance not only for clinical diagnostics, because it could serve as a predictor of depression [6], epilepsy [7] and schizophrenia [8] but also for quality control of this product in the manufacturing industry. Until now, different methods for taurine determination have been developed using mass spectrometry [9], fluorescence [10], spectrophotometry [11] and electrochemistry [12, 13]. However, none has been reported to date using Electrochemiluminescence (ECL) for its quantification, despite the sensitivity of this method. In this process species generated on the surface of the electrode are subjected electron transfer reactions to form excited states that can produce light when

they return to the ground state. Therefore, it is necessary to use luminophore species, such as ruthenium or its derivatives complexes and a co-reactant as shown in Scheme 1.

Although there are a wide variety of molecules that exhibit ECL, the overwhelming majority of publications concerned with co-reactant ECL and its analytical applications are based on chemistry involving $[\text{Ru}(\text{bpy})_3]^{2+}$, or its derivatives, as the emitting species, because of their excellent chemical, electrochemical, and photochemical properties even in aqueous media and in the presence of oxygen [14].

To be a good ECL co-reactant, several criteria need to be met, which include solubility, stability, electrochemical properties, kinetics, quenching effect, ECL background, etc. Among these, the most important is the electrochemical properties of the co-reactant. The co-reactant should be easily oxidized or reduced with the luminophore species at/or near the electrode surface and undergo a rapid chemical reaction to form an intermediate, that has sufficient reducing or oxidizing energy to react with the oxidized or reduced luminophore to form the excited state. Amine-related systems have been widely employed [14] as co-reactants with $[\text{Ru}(\text{bpy})_3]^{2+}$ as luminophore. Taurine has an amine. Therefore, it can be both co-reactant and analyte simultaneously in an ECL assay for its determination. As far as we know this possibility has not addressed yet.

ECL intensity can be greatly improved by the use of nanostructures. Hence, different conductive nanoelements, such as carbon nanotubes or gold nanoparticles has been employed [15]. Recently, new nanomaterials as nanocrystal semiconductors, such as SiO_2 [16], quantum dots [17, 18] have also been employed providing excellent results, since the semiconductor nanoparticles can be electrochemical excited to generate the reduced or the oxidized states of nanoparticles, which can react with some co-reactants to produce ECL signals. In this sense, others nanostructures, such as ZnO nanowires, that have additional

properties as a broad bandgap energy of about 3.4 eV and a high excitation binding energy (60 meV) at room temperature [19] are excellent candidates to improve ECL performance. Although it has been previously reported that ZnO nanoparticles exhibited excellent catalytic effect on ECL investigation [20, 21], the effect and the potential of different ZnO nanostructures has not totally explored yet.

In this work, we have employed a new ZnO nanostructures, ZnO nanowires (ZnO NWs), to enhance the ECL response of a taurine sensor. In this case taurine is simultaneously the co-reactant and the analyte as is depicted in Scheme 1. Screen-printed electrodes of different materials have been modified with ZnO NWs. The developed ECL strategy is a fast, selective and sensitive new method for the determination of taurine.

2. Materials and methods

2.1 Chemicals

Tris(2,2-bipyridyl) dichlororuthenium(II) hexahydrate ($[\text{Ru}(\text{bpy})_3]^{2+}$), taurine $\geq 99\%$, 98% H_2SO_4 , $\text{NaOH} \geq 98\%$, sodium phosphate dibasic $\geq 99\%$, sodium phosphate monobasic monohydrate $\geq 99\%$ were purchased from Sigma-Aldrich. The aqueous solutions were prepared using Milli-Q water. Commercial food supplement L-Taurine was supplied by Prozis, Madeira, Portugal.

2.2 Instrumentation

Optical properties of the ZnO NWs dispersions were carried out in a double beam PharmaSpec UV-1700 series Shimadzu spectrophotometer operating from 200 nm to 1100 nm. Fluorescence emission spectroscopy was carried out on a Cary Eclipse Varian spectrofluorimeter. All measurements are performed using 1.0 cm path length quartz cuvettes. Every spectrum is referred to a blank sample containing pure solvent and are carried out at room temperature.

Raman spectroscopy experiments were carried out in a Confocal Raman spectrometer Bruker Senterra (Bruker Optic, Ettlingen, Germany) with a resolution from 3 to 5 cm^{-1} . Measurements were performed using a 532 nm excitation wavelength laser at 200 mW, 5 accumulations and an integration time of 0.5 s.

Scanning electron microscopy (SEM) images were registered using a Philips XL30 S-FEG microscope.

Electrochemical measurements were performed using a Metrohm Autolab potentiostat PGSTAT 30 analyzer controlled by GPES 4.9 software. Screen-printed graphene and gold electrodes (SPGrE and SPAuE, respectively) were supplied by DropSens, Metrohm. Counter electrode is carbon and gold respectively and both cases including a silver pseudoreference electrode.

All ECL experiments were carried out with a potentiostat/galvanostat (± 4 V DC potential range, ± 40 mA maximum measurable current) and with a Si-photodiode integrated in the ECL cell from Dropsens-Metrohm. The electrochemical cell has a real volume of 50 μL where the electrodes are confined. The ECL equipment was controlled by the specific software DropView 8400. The potentiostat is the instrument responsible for initiating the ECL reaction by applying pulses of voltage or current. The electrochemical and chemiluminescence responses are perfectly synchronized and displayed in real time. The ECL calibration curves were obtained in the presence of $7.0 \times 10^{-3} \text{ mol L}^{-1}$ $[\text{Ru}(\text{bpy})_3]^{2+}$. All the ECL experiments were performed at room temperature in the absence of light.

HPLC experiments were performed with a Varian 920LC liquid chromatograph with a PL-ELS 2100 Ice detector. HPLC separation was carried out on an Asahipak NH2P-50 (Shodex) column, operating column temperature 30°C. The mobile phase used was a gradient of Milli-Q water (A) and acetonitrile (B). Elution was carried out at a flow rate of 1.2 ml min^{-1} with

a gradient of A/B (%) as follows: 0 min, 25/75; 2 min, 25/75; 7 min, 35/65; 12 min, 35/65; 13 min, 25/25; 18 min 25/25. Detector conditions: misting and evaporation temperature was 30 °C and gas flow was 1.6 ml min⁻¹. The injection volume was 10 µl.

2.3 Procedures

2.3.1 Synthesis of ZnO nanowires (ZnO NWs)

ZnO NWs were synthesized on Si (1000) substrates by chemical vapor transport (CVT) in a horizontal quartz tube furnace by using Zn µm-size powder (5.5 N) and O₂ as solid and gas precursors, respectively, in an Ar carrier flux as thoroughly described elsewhere [22]. During the growth process, O₂ (g) react with the Zn (g) and formed a white product atop the substrate.

2.3.2 ZnO NWs sample preparation.

To integrate the ZnO NWs in the proposed sensor, the nanostructures are separated from the substrate by sonication and dispersed in H₂O. After drying out, the ZnO NWs powder is weighed and reimmersed in H₂O and further sonicated for 10 min. The resultant dispersion out of this process has a concentration 0.5 mg ml⁻¹. Each suspension is prepared before use.

2.3.3 ZnO NWs nanostructured screen-printed electrodes

Surfaces of both screen-printed graphene and gold electrodes were modified by drop casting with ZnO NWs 5.0 µL, 0.5 mg ml⁻¹. In the case of SPAuE a previous activation of its surface is needed by cyclic voltammetry in 0.5 mol L⁻¹ H₂SO₄, 10 cycles.

3. Results and discussion

3.1 Characterization of ZnO NWs.

In a previous work we demonstrated that synthesized ZnO NWs have diameters between 90 and 150 nm and lengths between 2.0 and 20.0 µm [22].

We have studied the optical properties of ZnO NWs dispersions. The UV-vis absorption spectrum in water presents a band around 373 nm (Figure S1A), as other ZnO nanostructures. Because of nano-dimensions, ZnO nanostructures samples exhibit a blue shifted absorbance peak as compared to their bulk counterpart showing an absorbance peak at 386 nm (3.2 eV) at room temperature [23-25].

The fluorescence spectrum when excited at 330 nm shows an emission peak at 384 and a broad one at 520 nm (Figure S1B). The first one is related to near band-edge (NBE) emission of the ZnO nanostructure, and is attributed to the recombination of free excitons by an exciton–exciton collision process [26]. The second one is attributed to different intrinsic defects such as oxygen vacancies, zinc vacancies, oxygen interstitials, zinc interstitials and oxygen antisites [27-31].

The Raman spectra of a sample of ZnO NWs aligned vertically on a silicon plate was recorded in the backscattering mode, using a laser with a wavelength of 532 nm and a power of 200 mW (Figure S1C). A predominant peak can be observed at 438 cm^{-1} corresponding to the E2 mode (high). The peak corresponding to the E2 mode (low) is also observed, and, less intense, the two E2 modes at 325 cm^{-1} . The peak at 380 cm^{-1} is assigned to the A1 (TO) mode and the peak at 513 cm^{-1} to the E1 (LO) mode. In this case, the E1 (LO) mode should not be observed, because of the configuration in which the measurement was carried out, but it is also associated with the presence of oxygen vacancies and interstitial Zn in the structure of ZnO [32].

3.2 Electrochemiluminescent determination of Taurine

The determination of taurine based on ECL was investigated using different electrochemical platforms: bare screen-printed graphene (SPGrE) or gold (SPAuE) electrodes and ZnO NWs nanostructured screen-printed electrodes.

3.2.1 Screen-printed graphene or gold electrodes

Figure 1 presents UV-vis and fluorescence spectra for the subsequent design of electrochemiluminescence experiments. Figure 1A shows the UV-vis absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the absence and in presence of taurine. In absence of taurine, the spectrum exhibits two absorption bands at 290 nm and 450 nm, respectively. The band at 450 nm is due to the metal-to-ligand charge transfer of $[\text{Ru}(\text{bpy})_3]^{2+}$ [33], whereas the absorption peak at 290 nm is a $\Pi\text{-}\Pi^*$ transition between the internal ligands. In presence of $5.0 \times 10^{-6} \text{ mol L}^{-1}$ of taurine no changes in these bands are observed.

The fluorescence spectra (Figure 1B) of $[\text{Ru}(\text{bpy})_3]^{2+}$ shows a band at 620 nm when the samples were excited at 450 nm. A very small increase in fluorescence intensity can be seen when taurine is in the solution compared to the ruthenium complex alone. No fluorescence is observed for a solution containing only taurine.

Electrochemical experiments have been also carried out for the characterization of $[\text{Ru}(\text{bpy})_3]^{2+}$ and taurine. Figure 1C shows cyclic voltammograms of $2.0 \times 10^{-2} \text{ mol L}^{-1}$ of taurine in 0.1 mol L^{-1} phosphate buffer pH 8.0 in the absence and in the presence of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of $[\text{Ru}(\text{bpy})_3]^{2+}$. As can be observed taurine has not electrochemical response in the potential range studied. In presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ a slight increase of the anodic current is observed compared to the $[\text{Ru}(\text{bpy})_3]^{2+}$ cyclovoltammetric response (red line), either for graphene or gold electrodes. This effect is indicative of an electrocatalytic process, in which the oxidized form of Ru is reduced back by the taurine in an EC mechanism, as it is depicted in Scheme 1. Voltammograms were carried out at different scan rates. Currents increased

linearly with the square root of scan rate, confirming that it corresponds to a diffusional process (Figure S2A). In addition, a plot of $I/v^{1/2}$ vs v shows the expected shape for an EC process (Figure S2B) according with that reported by Nicholson and Shain [34].

FIGURE 1

These preliminary results indicate that taurine could be a highly efficient co-reactant for $[\text{Ru}(\text{bpy})_3]^{2+}$ in an ECL process. Hence, ECL studies of taurine at both electrodes were carried out (Figure 2). SPGrEs give a high ECL signal intensity, due to their good electronic conductivity, high surface area and volume ratio (Figure 2A). However, a considerable increase in the ECL signal of up to three times units is observed when SPAuE is used (Figure 2B) compared to the results obtained with SPGrE. Even though gold is not luminescent, the high intensity of the ECL can be attributed to both its high electrical conductivity and excellent optical properties. The nature of the electrode plays an important role in the ECL process [14]. It has been demonstrated that in the ECL process of the system $[\text{Ru}(\text{bpy})_3]^{2+}$ /tri-n-propylamine (TPrA), the kinetic of the direct oxidation of TPrA was faster at hydrophobic gold surfaces, causing a significant increase in the intensity of ECL with respect to the modified hydrophilic electrode [35]. This behavior is similar to that observed for the system $[\text{Ru}(\text{bpy})_3]^{2+}$ /taurine at SPAuE (Figure 2B). In the present work, SPAuEs not only provide enhanced ECL signals for the luminescence of $[\text{Ru}(\text{bpy})_3]^{2+}$ and taurine, but also a faster response. Moreover, a lower overpotential is required to obtain high ECL (see Figure 2B).

FIGURE 2

Several parameters have been examined for the optimization of the experimental conditions of the ECL for the system $[\text{Ru}(\text{bpy})_3]^{2+}$ /Taurine at SPAuE (Figure S3). ECL is very sensitive to the pH of the solution [36]. Therefore, the ECL intensity as a function of pH was studied at different pHs. pH 8.0 provides the higher ECL intensity (Figure S3A), as occurs with tri-n-propylamine [37] and glyphosate [35]. This may be explained considering that in aqueous solution the taurine molecule is involve in an acid-base equilibrium with two different ionic forms. At pH 8.0 part of the amine is deprotonated, which is the most ECL active form.

The concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ was also optimized keeping constant the taurine concentration. An increase in the ECL signal is observed until $7.0 \times 10^{-3} \text{ mol L}^{-1}$ $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure S3B). For concentrations higher than $7.0 \times 10^{-3} \text{ mol L}^{-1}$ $[\text{Ru}(\text{bpy})_3]^{2+}$, ECL intensity values remain constant.

The third parameter studied has been the scan rate. The ECL intensity reaches a maximum at 0.010 V s^{-1} and then decreases until a constant value, since there is a mass transport limitation (Figure S3C). Hence, experimental conditions selected for subsequent experiments were 0.1 mol L^{-1} phosphate buffer pH 8.0, $7.0 \times 10^{-3} \text{ mol L}^{-1}$ of $[\text{Ru}(\text{bpy})_3]^{2+}$ and scan rate of 0.010 Vs^{-1} .

3.2.2 ZnO NWs Nanostructured electrodes

ZnO NW is a semiconductor nanomaterial with a bandgap energy of about 3.4 eV. From the bibliography it is also known that ZnO nanoparticles exhibited a photoluminescent behavior due to the recombination of excitons and the defects in ZnO nanoparticles [38-42]. Previous works demonstrated that ZnO nanopowder and ZnO nanorods have improved the traditional ECL systems, which can be used for the determination of several analytes [43, 44]. These previous results suggest that ZnO nanostructures have promising application in ECL

investigations. In addition, it is not well established how the size and shape of the nanostructure may affect the ECL response and the use of larger size semiconductor nanoparticles has been rarely reported.

In this work, in order to improve the developed ECL system, the electrode surfaces were nanostructured by modification with ZnO NWs as is described in the experimental section. The resulting nanostructured electrodes were characterized by CV and SEM. Figure 3A shows CVs of a screen-printed gold electrode before and after modification with ZnO NWs (ZnO NWs/SPAuE) in 0.5 mol L⁻¹ H₂SO₄. Before modification, the typical oxidation and reduction processes of gold are observed. Upon the deposition of increasing concentrations of ZnO NWs, the intensity of the redox signals decreases, indicating that nanostructures are immobilized on the electrode surface. The electroactive area of the bare SPAuE is 0.27 cm². The maximum coating obtained was when 50.0 µg ZnO NWs were deposited on the electrode surface, resulting in an electroactive area of 0.05 cm². The total electroactive area was calculated by the integration of the gold oxide reduction peak, taking into account the equivalence of a load of -482 µC/cm² for the reduction of a monolayer of gold oxide [45]. Figure 3B and 3C show SEM images of both a bare SPAuE and a ZnO NWs modified SPAuE, respectively. It can be seen that, after ZnO NWs modification, the characteristic nanowires with an average length approximately of 1 µm dispersed on the gold surfaces are clearly observed.

FIGURE 3

When these ZnO NWs/SPAuEs are employed in the same ECL system described above for the determination of taurine, we observed that the presence of ZnO NWs improves the ECL

signal (Figure S4). A maximum of ECL intensity was obtained after modifying the SPAuE with 2.5 μg of ZnO NWs, which gives a surface coverage of 0.17 cm^2 , being exposed approximately the 64 % gold electrode (respect to the electroactive area). If the amount of ZnO NWs deposited on SPAuE increases, the intensity of ECL decreases. This is probably due to high coatings of ZnO NWs produce light scattering and therefore reduce the intensity of ECL [43].

The SPGrEs were also nanostructured with ZnO NWs and employed in the same ECL system than that described above for the ZnO NWs/SPAuE. Nevertheless, the ECL intensity obtained using ZnO NWs/SPAuE is substantially higher than those obtained with ZnO NWs/SPGrEs (Figure 4). These three-dimensional nanostructures increase the relative electrode surface area and improve the electronic conductivity, which in turn enhance the ECL produced. It has been widely employed the coupling of nanostructures with different kind of electrode surfaces in different ECL approaches. Among others, nanoparticles [46], nanotubes [47, 48] and nanorods [49] or the combination of several of them [50-52] with synergistic properties have been employed, resulting in the ECL enhancement. In addition to different kind of nanoparticles named above, other semiconductor nanostructures have recently been developed and tested to enhance the capabilities of ECL based techniques. In particular, recent results have been obtained with SiO_2 nanoparticles [53], MoS_2 [54] or quantum dots [55].

FIGURE 4

3.3 Taurine sensor: Linear response, sensitivity and stability

To evaluate the linear response range and sensitivity of the proposed taurine ECL sensors, ECL intensities were recorded after the addition of increasing concentrations of taurine to the solution under the optimal experimental conditions. Calibration curves have been obtained for the four electrochemical platforms studied: SPAuE, ZnO NWs/SPAuE, SPGrE and ZnO NWs/SPGrE. It can be observed that, in all cases, the ECL intensity increases on increasing taurine concentration (see Figure 5) in the range from 0 to 1mM.

FIGURE 5

The summary of the analytical parameters obtained for the taurine determination on the four electrochemical platforms developed are shown in Table 1. A clear difference is observed in the sensitivity, calculated from the slope of the calibration curve, for the different electrochemical platforms assayed. SPAuEs present a higher sensitivity than graphene ones. It should be noted that the presence of ZnO NWs gives to a higher sensitivity for both gold and graphene electrodes. This increase in sensitivity is 14% in the case of gold and of 31% in the case of graphene. The detection and quantification limits were calculated as the concentration of taurine that gave a signal equal to 3 or 10 times the standard deviation of background ECL response, respectively. The lowest detection limit obtained in this work for the determination of taurine by ECL was to be $5.5 \times 10^{-6} \text{ mol L}^{-1}$ with ZnO NWs/SPAuE. This value is comparable to that found by other electrochemical method developed by us, based on a disposable electrochemical detector in an HPLC system [13]. In addition, comparing our results with those obtained for other amino acids that have structures similar to taurine, the detection limits reported are similar ($5.5 \times 10^{-6} \text{ mol L}^{-1}$ and $10 \times 10^{-6} \text{ mol L}^{-1}$ for lysine and valine, respectively) [56].

TABLE 1

The reproducibility was evaluated from three different sensors for 5.0×10^{-4} mol L⁻¹ taurine determination. The relative standard deviation was calculated as 7.6, 6.5, 16.8 and 12.4 % for SPAuE, ZnO NWs/SPAuE, SPGrE and ZnO NWs/SPGrE, respectively. This indicates that the method using the ZnO NWs/SPAuE is more accurate than the rest of the platforms. Again, the presence of ZnO NWs give better response if we compare them with the results obtained without ZnO NWs.

From the above results and due to its excellent properties, it can be concluded that the best electrochemical platform to be used as taurine sensor is the ZnO NWs/SPAuE. Therefore, it was selected for following experiments.

To test the stability of the sensor, ECL signals of consecutive cycles from 0 to 1.3 V in 0.1 mol L⁻¹ phosphate buffer pH 8.0 containing 7.0×10^{-3} mol L⁻¹ [Ru(bpy)₃]²⁺ and 5.0×10^{-3} mol L⁻¹ taurine were evaluated. As can be seen in Figure 6, the response remains almost constant obtaining a relative standard deviation between successive measurements lower than 5%. The developed sensor has high stability to carry out taurine determination by ECL.

FIGURE 6

In addition, the storage stability of ZnO NWs/SPAuE was verified performing daily measurements for 28 days. The ZnO NWs/SPAuE kept 95.5 % of the initial ECL response. This result indicates that only a 4.5 % loss occurs, which indicates a minimum leakage of ZnO NWs from the surface of the SPAuE, keeping its electrochemiluminescent properties.

Based on the above results, the analytical parameters of our sensor are adequate for quality control of taurine in the food industry.

3.4 Taurine determination in a real sample

The use of sensors in the food industry is increasingly widespread. Not only to guarantee a safe and quality product production, but also as a process control tool that gives companies greater sustainability, efficiency and effectiveness in their production. Here, we have employed the developed sensor (ZnO NWs/SPAUE) for the determination of taurine as a control system capable of evaluating the purity of a commercial taurine supplement. Therefore, the sample was dissolved directly in 0.1 mol L⁻¹ phosphate buffer pH 8. The purity of taurine in the sample was determined directly by interpolating the ECL responses measured for the diluted samples through the calibration curve and the result obtained was 92±2 %. To validate our system, the purity of the commercial sample was also evaluated by high performance liquid chromatography (HPLC) as a comparative method. The purity obtained from the same sample was 95±1 %. As we can see, the average taurine concentration value obtained for three measurements using different sensors agrees well with that obtained by HPLC method demonstrating that ECL can be used for the determination of taurine in real samples.

Conclusions

In this work we developed a novel ECL taurine sensor based on the system taurine/[Ru(bpy)₃]²⁺ combined with ZnO NWs. Taurine has an amine group therefore is used as co-reactant in the ECL system, providing reliable detection of taurine at low concentrations and cost. ZnO NWs enhanced the ECL property. Single-use disposable electrodes and portable,

miniaturized and comfortable to transport equipment were employed, demonstrating that the ECL sensor developed is a fast, selective and sensitive method for the determination of taurine in real samples. Hence, it has been applied for the control food quality by analyzing the purity of a commercial taurine supplement. Results were validated by comparison with HPLC.

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Figure Captions

Scheme 1. Proposed ECL Reaction Mechanism of Ruthenium and Taurine.

Figure 1. (A) UV–vis absorption spectra and (B) fluorescence emission spectra of 5.0×10^{-5} mol L⁻¹ of taurine (black line), 2.0×10^{-5} mol L⁻¹ of [Ru(bpy)₃]²⁺ (red line) and a mixture of both (blue line) in 0.1 mol L⁻¹ phosphate buffer pH 8.0. (C) Cyclic voltammetric response of a SPGrE in 0.1 mol L⁻¹ phosphate buffer pH 8.0 (inset) and in the presence of 2.0×10^{-2} mol L⁻¹ of taurine (black line) or 2.0×10^{-3} mol L⁻¹ of [Ru(bpy)₃]²⁺ (red line) or a mixture of both (blue line). Scan rate: $v = 0.050$ Vs⁻¹.

Figure 2. ECL response at SPGrE (A) or SPAuE (B) in the presence of 2.0×10^{-2} mol L⁻¹ of taurine (black line) or 2.0×10^{-3} mol L⁻¹ of [Ru(bpy)₃]²⁺ (red line) or a mixture of both (blue line) in 0.1 mol L⁻¹ phosphate buffer pH 8.0. Scan rate: $v = 0.050$ Vs⁻¹.

Figure 3. (A) Cyclic voltammetric response in 0.5 mol L⁻¹ H₂SO₄ at SPAuE incubated different amounts of ZnO NWs (0, 2.5, 5.0, 12.5, 25, 50.0 µg). Scan rate: 0.100 V s⁻¹. SEM images of bare SPAuE (B) and ZnO NWs/SPAuE, 5.0 µl, 0.5 mg ml⁻¹ (C).

Figure 4. ECL response at ZnO NWs/SPGrE (black line) and ZnO NWs/SPAuE (red line) in 0.1 mol L⁻¹ phosphate buffer pH 8 in the presence of 7.0×10^{-3} mol L⁻¹ [Ru(bpy)₃]²⁺ and 5.0×10^{-3} mol L⁻¹ taurine. Scan rate: $v = 0.010$ Vs⁻¹.

Figure 5. Sensor responses obtained from ECL measurements (n=3) for SPGrE (a), ZnO NWs/SPGrE (b), SPAuE (c) and ZnO NWs/SPAuE (d) in 0.1 mol L⁻¹ phosphate buffer pH 8 of various taurine concentrations and 7.0×10^{-3} mol L⁻¹ [Ru(bpy)₃]²⁺. The correlation coefficients obtained were 0.989, 0.996, 0.995 and 0.995, respectively. Scan rate: $v = 0.010$ V s⁻¹.

Figure 6. ECL response at ZnO NWs/SPAuE measured through continuous cycles in 0.1 mol L⁻¹ phosphate buffer pH 8.0 containing 7.0x10⁻³ mol L⁻¹ [Ru(bpy)₃]²⁺ and 5.0x10⁻³ mol L⁻¹ taurine. Scan rate: $\nu = 0.010 \text{ V s}^{-1}$.