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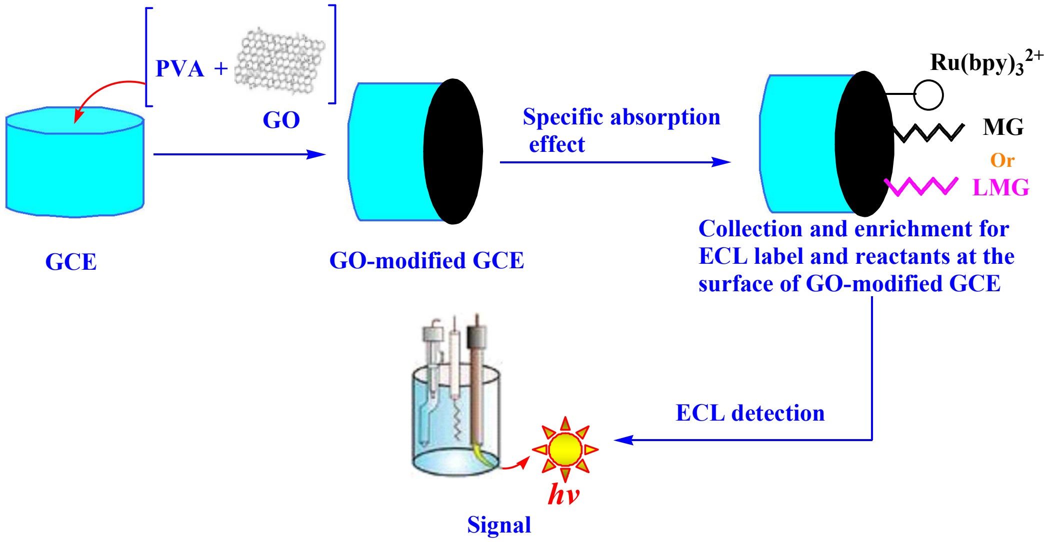
Graphical Abstract



An electrochemiluminescence (ECL) method for determination of malachite green (MG) and leucomalachite green (LMG) has been established based on ECL of $Ru(bpy)_3^{2+}$ at the GO-modified GCE.

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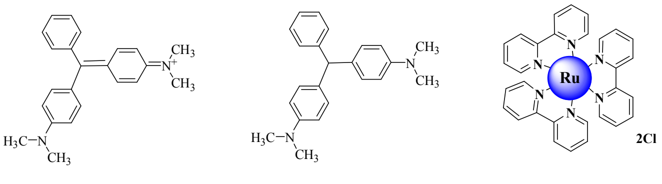
Determination of malachite green and leucomalachite green based on electrochemiluminescence of Ru(bpy)$_3^{2+}$ at graphene oxide modified glassy carbon electrodes

Jiantao Shao,[a] Yunmeng Zhao,[b] Fengyu Liu,*[a] Wei Li[a] and Yulong Gao[a]

The graphene oxide (GO) modified glassy carbon (GC) electrode has been employed for the determination of malachite green (MG) and leucomalachite green (LMG) based on the electrochemiluminescence (ECL) of Ru(bpy)$_3^{2+}$. It gave a linear response over a concentration range of 1.0×10^{-16}~1.0×10^{-12} mol•L^{-1} for both MG and LMG. A remarkable detection limit of 1.0×10^{-16} mol•L^{-1} can be reached for MG and LMG in 0.1mol•L^{-1} phosphate buffer (pH = 10), which is much lower compared to the other detection methods. To check its applicability, the proposed method was employed to the determination of MG and LMG spiked into pond water, giving a good reproducibility and stability. All these results show that it will be possible to develop an ECL detection procedure for MG/LMG at GO-modified GC electrodes.

Introduction

With the rapid growth of world population, the consumption of raised fish and shellfish is growing with each passing day.[1] Meanwhile, the use of prohibited substances in aquaculture industry has become one of the major safety issues.[2] Malachite green (MG, Scheme 1) is a member of the triphenylcarbenium salts, classified as triarylmethane dyes in the dyestuff industry. Considering its low cost, ready availability and high efficiency, MG has been widely used illegally as a topical fungicide and parasiticide.[3] However, more and more evidences showed that MG is potentially carcinogenic, teratogenic and mutagenic.[4-6]



Malachite Green (MG) Leuco Malachite Green (LMG) Ru(bpy)$_3^{2+}$

Scheme 1 Structures of MG, LMG and Ru(bpy)$_3^{2+}$.

Leucomalachite green (LMG, Scheme 1) could be readily formed by the metabolic reduction of MG in fish,[7] but LMG is considered to be more hazardous than MG, because the half-life of MG in fish muscle is approximately 70 hours, and LMG persists even longer in fish tissue.[8] Both MG and LMG are suspected carcinogenic and mutagenic agents, and MG has been banned in aquaculture operations in many countries including the United States, the European Union and China. Therefore, the monitor of MG and LMG has attracted particular attention from medical scientist, biologist, biochemist, and environmental chemist. In recent years, some methods have been utilized to measure MG and LMG, such as LC/MS (Liquid Chromatography/Mass Spectrometry)[9-11] Spectrophotometry,[12-14] RNA-Aptamer-Based Assay[15] and Raman Spectrometry[16] etc. However, it's still necessary to develop a simple but reliable detection method for the rapid and sensitive determination of MG and LMG. In our previous work,[17] the ECL of Ru(bpy)$_3^{2+}$ (Scheme 1) has been employed for determination of MG and LMG at Au electrode and it gave a linear response (R^2=0.9992) for MG concentration from 1.0×10^{-8}~1.0×10^{-5} mol•L^{-1} with a detection limit of 1.0×10^{-8} mol•L^{-1} in a borate buffer (pH = 10). Meanwhile, LMG was detected and the same detection limit was reached. These results provide a possibility of developing ECL method for the determination of MG and LMG.

To continue our research and further improve detecting efficiency, graphene oxide (GO) was chosen and immobilized on the glassy carbon (GC) electrodes, because GO has high Young's modulus and hardness, excellent flexibility, and low cost compared with carbon nanotubes, which make it an effective reinforcement for electrode composites.[18,19] In particular, GO is negatively charged and has many π-conjugated aromatic domain in its basal plane,[20-22]thus it is a remarkable material for strongly immobilizing substances that are positively charged and have aromatic structure through both electrostatic interaction and π-π stacking interaction.[23,24] PVA (polyvinyl alcohol) has been chosen as a membrane material and solvent for GO, due to the reason that there are a large number of hydrophilic groups on GO surface, such as hydroxyl, carboxyl and epoxy[25] which can form hydrogen bonds with the PVA chains that contain even more hydrophilic groups,[26, 27] enhancing the interfacial adhesion ability and the mechanical performance of the resulting PVA/GO composite.[28]

MG/LMG can be good candidates to interact with GO due to the specific aromatic structure. However, to our knowledge, the GO-modified GC electrode for the determination of MG and LMG has not been reported. To make a comparison with our previous work,[17] GO-modified GC electrode was utilized to determine MG and LMG based on the ECL of $Ru(bpy)_3^{2+}$. It gave a linear response over a concentration range of 1.0×10^{-16}~1.0×10^{-12} mol•L^{-1} for both MG and LMG. A remarkable detection limit of 1.0×10^{-16} mol•L^{-1} can be reached for MG and LMG in 0.1 mol•L^{-1} phosphate buffer (pH = 10). Which is much lower compared to the other detection methods. All these provided a possibility of developing GO-modified GC electrode for ECL determination of MG and LMG.

Experimental

Materials and Reagents

Cl^- salt of the parent $Ru(bpy)_3^{2+}$ was a sample left in our previous work.[29] MG and LMG were bought from Aldrich. GO was purchased from Nanjing XFNANO Materials Tech. Co., Ltd, China. PVA (polyvinyl alcohol, average M_w 17000, 99% hydrolyzed) was purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Other chemicals and solvents were obtained from commercial sources without further purification unless specifically mentioned.

Preparation of GO-modified glassy carbon electrode

GC working electrodes (3.0 mm in diameter) were first polished with a slurry of 0.05 mm alumina, then sonicated, and rinsed with deionized water. Then the electrode was successively sonicated in 1:1 nitric acid and doubly distilled water, and allowed to dry at room temperature. An amount of 0.75 mg of the treated GO[30] was dispersed with the aid of ultrasonic agitation in 5 mL deionized water, 1 mL was taken to mix with 2 mL 5% PVA aqueous solution, to obtain a homogeneous, well-distributed suspension, then 10 μL of this suspension was dropped onto the surface of the pretreated GC electrode, and the solvent was allowed to evaporate at room temperature in the air. Fig. 1 shows SEM images of the fracture surfaces of PVA and PVA/GO films. It is no doubt that GO-modified GC would increase the surface area of reaction and provide collection and enrichment effects on both the ECL labels and the determinands, which, as a result, improved the testing efficiency.

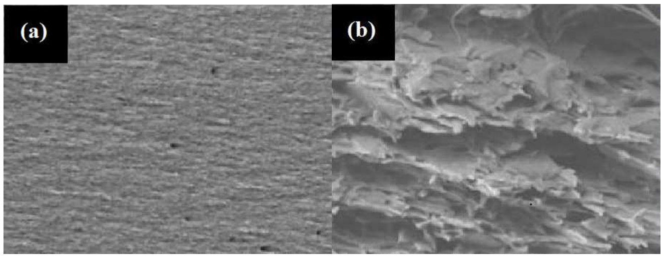


Fig. 1 SEM images of the fracture surfaces of pure PVA (a), and the composites of PVA/GO (b).

ECL measurement

ECL measurements were performed on MPI-B multifunctional ECL system from Xi'an Remex Analyse Instrument Co., Ltd., and the detecting method has been described elsewhere.[31-35] All experiments were carried out at room temperature. A KCl-saturated Ag/AgCl electrode and a platinum wire were used as the reference and the

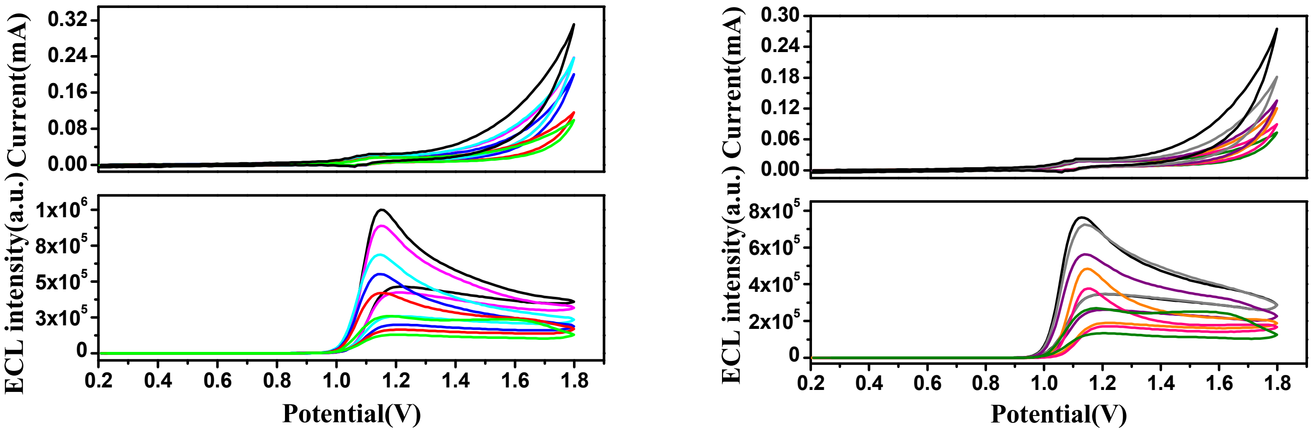


Fig. 2 left: Cyclic ECL and voltammetric curves of 1 mM Ru(bpy)$_3^{2+}$ and corresponding MG coreactant in 0.1 mol•L^{-1} phosphate buffer (pH = 10) at GO-modified GC electrode, Ru(bpy)$_3^{2+}$ alone (black line), addition of 1.0×10^{-16} mol•L^{-1} (magenta line), 1.0×10^{-15} mol•L^{-1} (cyan line) , 1.0×10^{-14} mol•L^{-1} (blue line), 1.0×10^{-13} mol•L^{-1} (red line) and 1.0×10^{-12} mol•L^{-1} (green line), respectively; scan rate: 100 mV•s^{-1}. **right:** Cyclic ECL and voltammetric curves of 1 mmol•L^{-1} Ru(bpy)$_3^{2+}$ and corresponding LMG coreactant in 0.1 mol•L^{-1} phosphate buffer (pH= 10) at GO-modified GC electrode, Ru(bpy)$_3^{2+}$ alone (black line), addition of 1.0×10^{-16} mol•L^{-1}(gray line), 1.0×10^{-15} mol•L^{-1} (purple line) ,1.0×10^{-14} mol•L^{-1} (orange line), 1.0×10^{-13} mol•L^{-1} (pink line) and 1.0×10^{-12} mol•L^{-1} (olive line), respectively; scan rate: 100 mV•s^{-1}.

auxiliary electrode, respectively. Ruthenium complex and corresponding MG/LMG additive were added into 0.1 M phosphate buffer (pH = 10), and then the mixture was transferred to an ECL detection cell. Cyclic potential sweep experiments were carried out in the potential region from 0.2 to 1.8 V and then back to 0.2 at a scan rate of 100 mV•s^{-1}, the ECL signals and CV vs time were measured repeatedly for at least 7 times, and the averaged readings were used for the creation of plots.

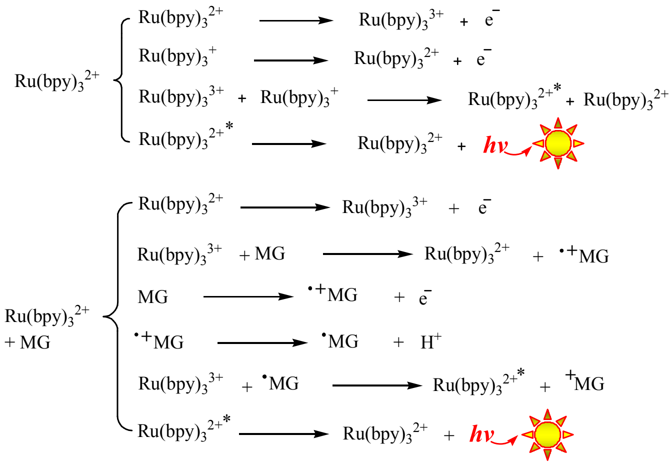
Results and discussion

Optimization of detection conditions

According to literature,[36,37] pH and scan rate can directly affect the ECL over a wide range. It is noted that both the highest ECL signal and the highest signal to background noise ratio were reached at pH = 10 in 0.1mol•L^{-1} phosphate buffer and the best reproducibility and stability were shown under the condition of 100 mV•s^{-1}. This is in good agreement with our previous work.[17] So, pH = 10 in 0.1 mol•L^{-1} phosphate buffer and scan rate 100 mV•s^{-1} were employed for all detections below.

Meanwhile, different concentrations of GO/PVA composite films were prepared by the same procedure, and the best reproducibility and stability can be achieved when utilizing 0.15 mg•mL^{-1} GO and 3.4% PVA to modify the GC electrode.

ECL performance of Ru(bpy)$_3^{2+}$ in the presence of MG and LMG at GO-modified GC electrodes



Scheme 2 Proposed ruthenium/MG ECL mechanism.

Cyclic voltammograms (CV) and the corresponding ECL performance of 1 mM Ru(bpy)$_3^{2+}$ for a certain amount of MG (left) and LMG (right) at the GO-modified GC electrodes are shown in Fig. 2. When the electrode potential was scanned positively (close to 1.08 V, Fig. S1), upon the oxidation of Ru(bpy)$_3^{2+}$, an ECL signal was observed. The anodic current increased along with the increasing of the oxidation potential, but significant ECL increasing was observed when the electrode potential was close to 0.95 V (Fig. S2-S3), where the MG and LMG were observed to be intensely oxidized at the GC electrode. Especially, the oxidation potential of $Ru(bpy)_3^{2+}$ is much higher than that of MG and LMG on the GC electrode (Fig. S1-S3), which is much in favor of the redox reaction between them. As a result, the ECL intensity increases along with the addition of MG/LMG into $Ru(bpy)_3^{2+}$.

According to the mechanism proposed in our previous work,[17] at the GC electrode, MG undergoes a one-electron oxidation, forming an MG cation radical $^{\bullet+}$MG, which was rapidly deprotonated to form MG free radicals $^{\bullet}$MG. This MG radical could be necessary to generate the excited state $Ru(bpy)_3^{2+*}$ through reduction of $Ru(bpy)_3^{3+}$ as shown in Scheme 2.

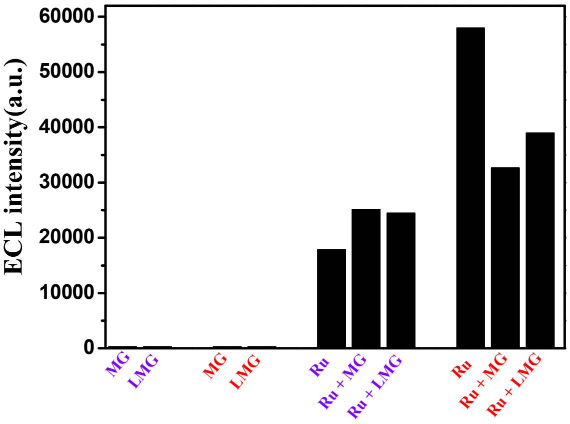


Fig. 3 ECL intensity of 1.0×10^{-12} mol•L^{-1} MG, 1.0×10^{-12} mol•L^{-1} LMG, 1.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$, 1.0×10^{-12} mol•L^{-1} MG + 1.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$, 1.0×10^{-12} mol•L^{-1} LMG + 1.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ in 0.1 mol•L^{-1} phosphate buffer (pH = 10) on GC (blue font) and GO-modified GC electrodes (red font).

It should be noted that ECL efficiency has a strong dependence on electrode material[38,39] and surfactants.[40-42] The ECL intensity of $Ru(bpy)_3^{2+}$ on the GO-modified GC electrode is much higher than that on the bare GC electrode as shown in Fig. 3, which can be ascribed to the collection and enrichment effect of GO-modified GC electrode on $Ru(bpy)_3^{2+}$ through electrostatic interaction.[43-45] As a modified electrode material, Graphene oxide (GO) is negatively charged and has many π-conjugated aromatic domain in its basal plane,[20] thus it is a remarkable material for strongly immobilizing substances that are positively charged and have aromatic structure through both electrostatic interaction and π-π stacking interaction.[46] $Ru(bpy)_3^{2+}$ is an alternative luminophore, which has a good absorption ability because bpy is a bidentate aromatic ligand through both electrostatic interaction and π-π stacking interaction.[36] The oxidation peak current of $Ru(bpy)_3^{2+}$ was significantly improved on the GO-modified GC electrode[47] and the ECL intensity was significantly enhanced (Fig. 3), due to high catalytic activity and conductivity of graphene. Moreover, GO can reduce the oxidation potential of $Ru(bpy)_3^{2+}$ as shown in Fig. S1.

All these indicate that GO can immobilize more $Ru(bpy)_3^{2+}$ on the surface of modified GC electrode than that at the bare GC electrode,[48] increase the surface area of reaction and provide collection and enrichment effects on both the ECL labels and the determinands. As a result, GO-modified GC improved the ECL testing efficiency and enhanced the ECL. These results are in agreement with the literature. [44, 49]

However, the ECL intensity decreased upon addition of MG/LMG into $Ru(bpy)_3^{2+}$ on the GO-modified GC electrode. This can be ascribed to the decrease of the oxidation potentials and the distribution status of $Ru(bpy)_3^{2+}$ and MG/LMG on the surface of GO-modified GC electrode. An obvious decreasing effect can be observed for the oxidation potentials of MG/LMG and $Ru(bpy)_3^{2+}$ on GO-modified GC electrode (Fig. S1-S3). As a consequence, the oxidation potential difference between $Ru(bpy)_3^{2+}$ and MG/LMG is decreased from 0.35/0.43 V to 0.09/0.40 V respectively, which is unfavorable to the redox reaction between $Ru(bpy)_3^{2+}$ and MG/LMG. On the other hand, the amount of $Ru(bpy)_3^{2+}$ on the surface of GO-modified GC electrode decreases with addition of MG/LMG because MG/LMG can be simultaneously immobilized on the higher specific surface of the GO-modified GC electrode through π-π stacking interaction. All these can result in a decreasing effect on ECL intensity as MG/LMG are spiked into $Ru(bpy)_3^{2+}$.

For 1 mM $Ru(bpy)_3^{2+}$ in 0.1 M phosphate buffer (pH = 10) at the GO-modified GC electrode, the ECL intensity of $Ru(bpy)_3^{2+}$ decreased with an increasing of the amount of MG and LMG. The ECL increase ($\Delta ECL = ECL_{\text{before addition of MG/LMG}} - ECL_{\text{after addition of MG/LMG}}$) versus the logarithmic concentration of MG/LMG was linear over an MG/LMG concentration range of $1.0\times10^{-16}\sim1.0\times10^{-12}$ mol•L^{-1}. As illustrated in Fig. 4 (MG, left) (slope = 147018; intercept

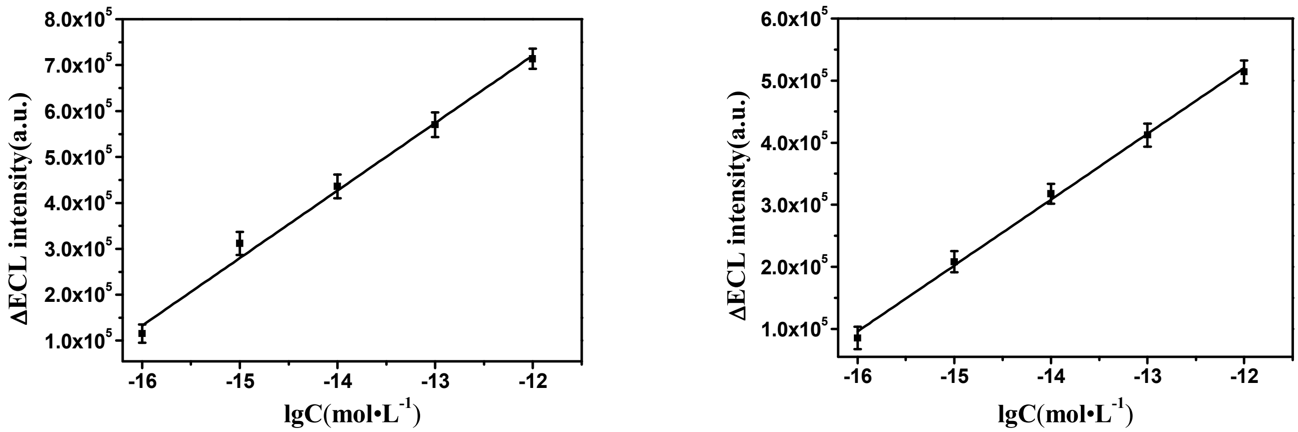


Fig. 4 Dependence of the ECL versus the logarithmic concentration of MG (left) and LMG (right) with 1 mM $Ru(bpy)_3^{2+}$ in 0.1 mol•L^{-1} phosphate buffer (pH = 10) at GO-modified GC electrodes.

= 2485250; correlation coefficient = 0.99238; n =5) and in Fig. 4 (LMG, right) (slope = 106168; intercept = 1794640; correlation coefficient = 0.99616; n = 5), both MG and LMG detection limit was further down to 1.0×10^{-16} mol•L^{-1} at a signal to noise ratio of three, which is 8 orders of magnitude lower than that at an Au electrode,[17] as well as much lower than that of the other detection methods.[9-11] It is concluded that MG and LMG could be determined quantitatively in a concentration range of 1.0×10^{-16}~1.0×10^{-12} mol•L^{-1} at the GO-modified GC electrodes.

To check the electrode reaction is rate controlling or a diffusion process,[50] we have studied the dependence of the ECL intensity and the anodic current vs. square root of scan rates ($v^{1/2}$), respectively. The result indicated that the anodic current varied linearly with the square root of the scan rate as shown in Fig. S4, demonstrating that the decisive factor for the redox reaction between $Ru(bpy)_3^{2+}$ and MG on the GO modified electrode surface was rate controlling.[51] However, the absolute ECL intensity value (ΔECL = $ECL_{\textbf{before addition of MG/LMG}}$ - $ECL_{\textbf{after addition of MG/LMG}}$) versus the logarithmic concentration of MG/LMG was linear over an MG/LMG concentration range of 1.0×10^{-16}~1.0×10^{-12} mol•L^{-1}. All these can be ascribed to the above mentioned complicated reasons such as the ECL increasing effect of $Ru(bpy)_3^{2+}$ on the GO-modified GC electrode, the decrease of the oxidation potentials and the competitive distribution status of $Ru(bpy)_3^{2+}$ and MG/LMG on the surface of GO-modified GCE.

Reproducibility and stability of the GO-modified GC electrode

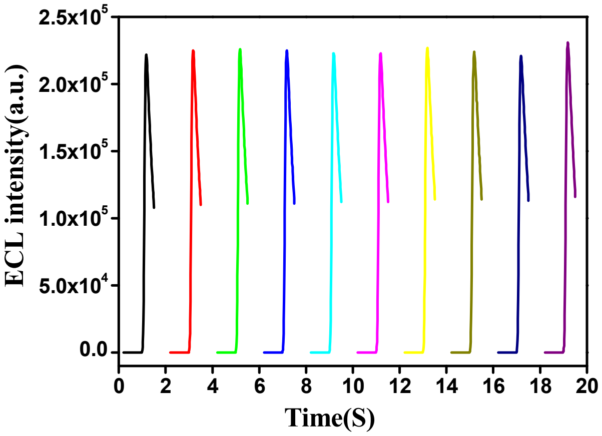


Fig. 5 Continuous cyclic scanning of GO-modified GC electrode for 10 cycles in pH = 10 phosphate buffer containing 1 mM $Ru(bpy)_3^{2+}$ and 1.0×10^{-13} mol•L^{-1} MG; The scan rate was 100 mV•s^{-1}.

To evaluate the reproducibility and stability of the ECL measurement on the GO-modified GC electrode, the ECL performance was studied by immersing the GO-modified GC electrode in 0.1 mol•L^{-1} phosphate buffer (pH = 10) containing 1 mM $Ru(bpy)_3^{2+}$ and 1.0×10^{-13} mol•L^{-1} MG, then continuously cyclic potential scanning for ten times at the scan rate of 100 mV•s^{-1} (Fig. 5). No significant change for the ECL intensity can be observed in the detection process, suggesting good reproducibility and stability of the ECL measurement on the GO-modified GC electrode. The same trend can be observed for 1 mM $Ru(bpy)_3^{2+}$ and 1.0×10^{-13} mol•L^{-1} LMG in 0.1 mol•L^{-1} phosphate buffer (pH = 10) under the same condition, further demonstrated the excellent reproducibility and stability of the GO-modified GC electrode.

Interference study

To further assess the proposed method for the analysis of MG in real samples, the interference from various cations and anions was investigated by studying their effects on the determination of MG. Solution containing of 1.0×10^{-12} mol•L^{-1} MG, 1.0×10^{-12} mol•L^{-1} LMG and various amounts of foreign ions were prepared and the general procedure was followed.[17,52] A species was considered not to interfere if it caused a relative error of less than ±5% in the measurement of 1.0×10^{-12} mol•L^{-1} MG and 1.0×10^{-12} mol•L^{-1} LMG. Concentrations of the interfering compounds relative to 1.0×10^{-12} mol•L^{-1} MG and 1.0×10^{-12} mol•L^{-1} LMG tolerated in their ECL detection were determined to be the following: one hundred million-fold of concentration, by weight, for KNO_3, $NaNO_3$, K_2CO_3, Na_2CO_3, KCl, NaCl, K_2SO_4, Na_2SO_4; five million-fold of concentration, by weight, for $Mg(NO_3)_2$, $MgCl_2$, $MgSO_4$; two hundred thousand-fold of concentration, by weight, for NH_4Cl, NH_4NO_3; ten thousand-fold of concentration, by weight, for glucose, fructose, quinolones, sulfonamides, cephalosporins etc. In short, this method was satisfactorily tolerant towards interference from several chemicals.

Application

In order to assess the applicability of the proposed method, 1.0×10^{-3} mol•L^{-1} $Ru(bpy)_3^{2+}$ was applied to the determination of the MG and LMG spiked into a pond water sample. The analytical results are shown in Table 1. It is noted that the recovery is quite satisfied at GO-modified GC electrodes. The RSDs of less than 5.48% for MG and LMG showed the fine accuracy, suggesting the absence of any interfering species on the ECL measurement, further demonstrated the applicability of this method.

Table 1 The recovery of MG and LMG spiked into a pond water sample detected by 1 mM $Ru(bpy)_3^{2+}$ in 0.1 M phosphate buffer (pH = 10) at GO-modified GC electrode[a].

Sample	Added (mol•L^{-1})	Detected (mol•L^{-1})	Average (mol•L^{-1})	Recovery	RSD[b]
MG	1.0×10^{-16}	0.97×10^{-16} 1.01×10^{-16} 0.99×10^{-16}	0.99×10^{-16}	99%	2.02%
	1.0×10^{-14}	1.01×10^{-14} 1.00×10^{-14} 1.00×10^{-14}	1.00×10^{-14}	100%	0.71%
	1.0×10^{-12}	1.02×10^{-12} 1.10×10^{-12} 0.99×10^{-12}	1.04×10^{-12}	104%	5.48%
LMG	1.0×10^{-16}	1.02×10^{-16} 0.99×10^{-16} 1.01×10^{-16}	1.01×10^{-16}	101%	1.57%
	1.0×10^{-14}	0.98×10^{-14} 1.01×10^{-14} 0.97×10^{-14}	0.99×10^{-14}	99%	2.14%
	1.0×10^{-12}	1.02×10^{-12} 0.99×10^{-12} 1.01×10^{-12}	1.01×10^{-12}	101%	1.57%

[a] Average of three samples, each sample was measured repeatedly for at least seven times, and the averaged readings were used. Applied potential: 0.2-1.8 V (vs. Ag/AgCl); Scan rate: 100 mV•s^{-1}.
[b] RSD, relative standard deviation.

Conclusions

In summary, the GO-modified GC electrode has been successfully employed for the determination of MG and LMG in pond water based on ECL of $Ru(bpy)_3^{2+}$. The detection limit is much lower than that of the other detection methods, and the recovery is quite satisfied with good reproducibility and stability. All these results provide the possibility of developing an ECL method for detecting MG and LMG at GO-modified GC electrodes.

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Notes and references

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1 J. Jacquet, J. Hocevar, S. Lai, P. Majluf, N. Pelletier, T. Pitcher, E. Sala, R. Sumaila, D. Pauly, *Oryx*, 2009, **44**, 45.
2 U.S. Food and Drug Administration, FAS-China fishery productsannual report 2007. http://www.thefishsite.com/articles/341/china-Fishery-productsannual-report-2007, 2008, [accessed:19 September 2011].
3 A. Stammati, C. Nebbia, I. De Angelis, A. G. Albo, M. Carletti, C. Rebecchi, F. Zampaglioni, M. Dacasto, *Toxicol. in Vitro.*, 2005, **19**, 853.
4 S. J. Culp, F. A. Beland, R. H. Heflich, R. W. Benson, L. R. Blankenship, P. J. Webb, P. W. Mellick, R. W. Trotter, S. D. Shelton, K. J. Greenlees, M. G. Manjanatha, *Mutation Research*, 2002, **506-507**, 55.
5 P. A. Soloman, C. A. Basha, M. Velan, N. Balasubramanian, *Chem. Biochem. Eng. Q.*, 2010, **24**, 445.
6 S. Srivastava, R. Sinha, D. Roy, *Aquat. Toxicol.*, 2004, **66**, 319.
7 W. C. Andersen, S. B. Turnipseed, J. E. Roybal, *J. Agric. Food Chem.*, 2006, **54**, 4517.
8 K. Halme, E. Lindfors, K. Peltonen, *J. Chromatogr. B*, 2007, **845**, 74.
9 G. Y. Chen, S. Miao, *J. Agric. Food Chem.*, 2010, **58**, 7109.
10 M. J. Martínez Bueno, S. Herrera, A. Uclés, A. Agüera, M. D. Hernando, O. Shimelis, M. Rudolfsson, A. R. Fernández-Alba, *Anal. Chim. Acta*, 2010, **665**, 47.
11 J. B. Lee, H. Y. Kim, Y. M. Jang, J. Y. Song, S. M. Woo, M. S. Park, H. S. Lee, S. K. Lee, M. Kim, *Food Addit. Contam. Part A*, 2010, **27**, 953.
12 A. Afkhami, R. Moosavi, T. Madrakian, *Talanta*, 2010, **82**, 785.
13 N. Pourreza, Sh. Elhami, *Anal. Chim. Acta*, 2007, **596**, 62.
14 I. Safarik, M. Safarikova, *Water Res.*, 2002, **36**, 196.
15 S. L. Stead, H. Ashwin, B. Johnston, J. A. Tarbin, M. Sharman, J. Kay, B. J. Keely, *Anal. Chem.*, 2010, **82**, 2652.
16 L. X. Quang, C. Lim, G. H. Seong, J. Choo, K. J. Do, S. K. Yoo, *Lab on a Chip*, 2008, **8**, 2214.
17 F. Y. Liu, X. Yang, Y. Q. Zhao, S. G. Sun, *Anal. Methods*, 2013, **5**, 660.
18 H. Q. Chen, M. B. Muller, K. J. Gilmore, G. G. Wallace, D. Li, *Adv. Mater.*, 2008, **20**, 3557.
19 K. C. Lin, S. Y. Lai, S. M. Chen, *Analyst,* 2014, **139**, 3991.
20 S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.*, 2007, **7**, 3394.
21 M. A. Raj, S. A. John, *Anal. Methods,* 2014, **6**, 2181.
22 R. A. Dar, N. G. Khare, D. P. Cole, S. P. Karna, A. K. Srivastava, *RSC Adv.,* 2014, **4**, 14432.
23 M. Pumera, Chem. *Soc. Rev.*, 2010, **39**, 4146.
24 L. Z. Yan, C. J. Lei, Y. F. Liu, Q. Hao, H. X. Ju, *Anal. Chem.*, 2013, **85**, 8001.
25 H. He, T. Riedl, A. Lerf, J. Klinowski, *J. Phys. Chem.*, 1996, **100**, 19954.
26 S. Y. Deng, H. X. Ju, *Analyst*, 2013, 138, 43.
27 H. F. Dong, C. Wang, Y. Xiong, H. T. Lu, H. X. Ju, X. J. Zhang, Biosens. Bioelectron., 2013, 41, 384.
28 L. Q. Liu, A. H. Barber, S. Nuriel, H. D. Wagner, *Adv. Funct. Mater.*, 2005, **15**, 975.
29 H. J. Li, F. Y. Liu, S. G. Sun, J. Y. Wang, Z. Y. Li, D. Z. Mu, B. Qiao and X. J. Peng, *J. Mater. Chem. B*, 2013, **1**, 4146.
30 I. Tantis, G. C. Psarras, D. Tasis, *Express Polym. Lett.*, 2012, **6**, 283.
31 S. G. Sun, Y. Yang, F. Y. Liu, Y. Pang, J. L. Fan, L. C. Sun, X. J. Peng, *Anal. Chem.*, 2009, **81**, 10227.
32 S. G. Sun, Y. Yang, F. Y Liu, J. L. Fan, X. J. Peng, J. Kehr, L. C. Sun, *Dalton Trans.*, 2009, 7969.
33 S. G. Sun, Y. Yang, F. Y Liu, J. L. Fan, J. Kehr, L. C. Sun, X. J. Peng, *Dalton Trans.*, 2010, **39**, 8626.
34 J. G. Li, Q. Y. Yan, Y. L. Gao, H. X. Ju, *Anal. Chem.*, 2006, **78**, 2694.
35 J. Li, J. P. Lei, Q. B. Wang, P. Wang, H. X. Ju, *Electrochim. Acta,* 2012, **83**, 73.
36 M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003.
37 L. H. Guo, F. F. Fu, G. N. Chen, *Anal. Bioanal. Chem.*, 2010, **399**, 3323.
38 Y. Zu, A. J. Bard, *Anal. Chem.*, 2000, **72**, 3223.
39 W. J. Miao, J. P. Choi, A. J. Bard, *J. Am. Chem. Soc.,* 2002, **124**, 14478
40 Y. Zu, A. J. Bard, *Anal. Chem.*, 2001, **73**, 3960.
41 P. M. McCord, A. J. Bard, *J. Electroanal. Chem.*,1991, **318**, 91.
42 D. Bruce, J. McCall, M. M. Richter, *Analyst*, 2002, **127**, 125.
43 F. Y. Liu, X. Yang, Y. Q. Zhao, *Analyst*, 2011, **136**, 374.
44 X. B. Li, G. R. Xu, X. Y. Jiang, J. Z. Tao, *J. Electrochem. Soc.,* 2014, **161**, H464.
45 D. Chen, L. H. Tang, J. H. Li, *Chem. Soc. Rev.,* 2010, **39**, 3157.
46 M. Pumera, *Chem. Soc. Rev.,* 2010, **39**, 4146.
47 M. Zidan, R. M. Zawawi,M. Erhayem, A. Salhin, I*nt. J. Electrochem. Sci.*, 2014, **9**, 7605.
48 Y. L. Yuan, H. J. Li, S. Han, L. Z. Hu, S. Parveen, H. R. Cai, G. B. Xu, *Anal. Chim. Acta*, 2012, **720**, 38.
49 F. Y. Liu, Y. L. Gao, W. Li, J. T. Shao, *RSC Adv.,* 2014, **4**, 34003.
50 A. Pietrzyk, W. Kutner, R. Chitta, M. E. Zandler, F. D'Souza, F. Sannicolò, P. R. Mussini, *Anal. Chem.*, 2009, **81**, 10061.
51 M. Vilas-Boas, E. M. Pereira, C. Freire, A. R. Hillman, *J. Electroanal. Chem.*, 2002, **538-539**, 47.
52 Z. Y. Guo, P. P. Gai, T. T. Hao, J. Duan, S. Wang, *J. Agric. Food Chem.,* 2011, **59**, 5257.