Solid-state electrochemiluminescence of tris(2,2′-bipyridyl) ruthenium

Hui Wei, Erkang Wang

Electrochemiluminescence (ECL) of tris(2,2′-bipyridyl)ruthenium [$Ru(bpy)_3^{2+}$] has received considerable attention. By immobilizing $Ru(bpy)_3^{2+}$ on an electrode surface, solid-state ECL provides several advantages over solution-phase ECL, such as reducing consumption of expensive reagent, simplifying experimental design and enhancing the ECL signal.

This review presents the state of the art in solid-state ECL of $Ru(bpy)_3^{2+}$. It briefly covers the mechanism of ECL of $Ru(bpy)_3^{2+}$, some recent developments in fabrication of solid-state ECL sensors, analytical applications of ECL and alignment of ECL with capillary electrophoresis (CE), microchip CE, flow-injection analysis, high-performance liquid chromatography. It also indicates the outlook in this field.

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1. Introduction

Electrochemiluminescence [1] (also called electrogenerated chemiluminescence, abbreviated as ECL) is a means of converting electrochemical energy into radiative energy at the surface of an electrode via an applied potential. Luminescent signals can be obtained from the excited states of an ECL luminophore generated at electrode surfaces during the electrochemical reaction. Among many organic and inorganic ECL systems, ECL based on inorganic compound tris(2,2′-bipyridyl) ruthenium(II) [$Ru(bpy)_3^{2+}$] has received considerable attention due to its importance to, for example, clinical tests and biomolecule detection. $Ru(bpy)_3^{2+}$ ECL has several advantages in different analytical areas, such as strong luminescence and good solubility in a variety of aqueous and non-aqueous solvents, inherent sensitivity, and wide linear range.

Since the first detailed studies of $Ru(bpy)_3^{2+}$ ECL were realized in solution [2], solution-phase ECL has been extensively studied. Unlike most chemiluminescent reagents, $Ru(bpy)_3^{2+}$ can be regenerated during the ECL reaction (as described in the mechanism section, below). As a result, solid-state ECL can be realized by immobilizing ECL reagent $Ru(bpy)_3^{2+}$ on an electrode surface. Compared with solution-phase ECL, solid-state ECL has several advantages, such as reducing the consumption of expensive ECL reagent $Ru(bpy)_3^{2+}$, simplifying experimental design, and enhancing the ECL signal. As a result, a growing number of different methods have been employed to fabricate solid-state ECL sensors by immobilizing $Ru(bpy)_3^{2+}$ on a solid surface, such as sol-gel entrapment, electrostatic attachment, layer-by-layer self-assembly and the Langmuir-Blodgett technique. Quite a lot of new materials, including cation-exchange polymers, silica nanoparticles (NPs), carbon nanotubes (CNTs), and metal NPs have also been developed for solid-state ECL. Many assays have been realized using solid-state ECL sensors. However, the solid-state ECL sensor itself can hardly be used for multi-analyte detection due to its poor selectivity. This drawback can be overcome by coupling with separation techniques, such as capillary electrophoresis (CE), microchip CE, flow-injection analysis (FIA) and high-performance liquid chromatography (HPLC). Much progress has been made in this field.

To date, there have been more than 1000 scientific publications (including papers, patents and book chapters) on ECL, and there have also been some excellent reviews [1,3–12] However, no
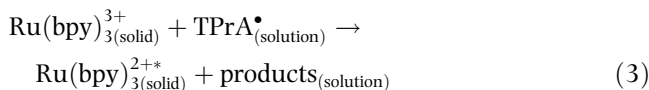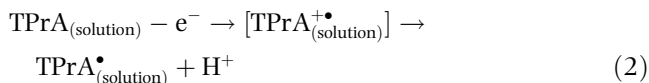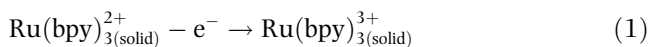
review has focused on solid-state ECL, so we present the state of the art of solid-state ECL and focus mainly on papers published after 2000.

2. Mechanisms of solid-state ECL of $Ru(bpy)_3^{2+}$

The mechanisms of ECL of $Ru(bpy)_3^{2+}$ have been extensively studied and well summarized [1]. Here, we give just a brief description of the ''oxidative-reductive'' reaction for solid-state ECL, in which $Ru(bpy)_3^{2+}$ is regenerated in situ at the electrode surface during the ECL process. As in ''oxidative-reductive'' ECL in solution, the solid-state ECL signal results when a co-reactant in solution reacts with $Ru(bpy)_3^{2+}$ immobilized on an electrode. Though a lot of substances (e.g., amino acids, oxalate, and DNA) could be used as co-reactants, tri-n-propylamine (TPrA) has been studied most, so we use TPrA to elucidate the mechanism of solid-state ECL.

When electrochemical stimulation is applied to the system, $Ru(bpy)_3^{2+}$ immobilized on the electrode is oxidized to $Ru(bpy)_3^{3+}$, then $Ru(bpy)_3^{3+}$ can be further reduced with co-reactant (e.g., TPrA) to produce excited state $Ru(bpy)_3^{2+*}$. ECL signals are obtained when $Ru(bpy)_3^{2+*}$ decays to ground-state $Ru(bpy)_3^{2+}$ (see the scheme below) [1].

$$Ru(bpy)_{3(solid)}^{2+} - e^- \rightarrow Ru(bpy)_{3(solid)}^{3+} \qquad (1)$$

$$TPrA_{(solution)} - e^- \rightarrow [TPrA_{(solution)}^{+\bullet}] \rightarrow$$
$$TPrA_{(solution)}^{\bullet} + H^+ \qquad (2)$$

$$Ru(bpy)_{3(solid)}^{3+} + TPrA_{(solution)}^{\bullet} \rightarrow$$
$$Ru(bpy)_{3(solid)}^{2+*} + products_{(solution)} \qquad (3)$$

$$Ru(bpy)_{3(solid)}^{2+*} \rightarrow Ru(bpy)_{3(solid)}^{2+} + h\nu \qquad (4)$$
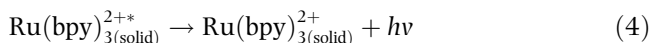
As shown in the scheme above, ECL signal intensity is positively related to the concentration of $Ru(bpy)_3^{2+}$ or the co-reactant, so ECL can be used to detect both. In solid-state ECL, since $Ru(bpy)_3^{2+}$ is immobilized on the electrode surface, the concentration of $Ru(bpy)_3^{2+}$ is constant, so the concentration of co-reactants can be determined by measuring the intensity of the ECL emission.

3. Immobilization matrices for solid-state ECL of $Ru(bpy)_3^{2+}$

To fabricate solid-state ECL sensors, $Ru(bpy)_3^{2+}$ needs to be immobilized on the electrode surface. Since the early report of immobilization of $Ru(bpy)_3^{2+}$ on an electrode surface using Nafion by Rubinstein and Bard [13], quite a number of different methods and materials have been developed to immobilize $Ru(bpy)_3^{2+}$. Though much progress has been made in this field, new immobilization methods and materials are still needed to make robust, novel, sensitive and regenerative solid-state ECL sensors.

3.1. Cation-exchange polymer

Bard's early work for solid-state ECL using cation-exchange polymer Nafion has been extended by many researchers [14–28]. Though $Ru(bpy)_3^{2+}$ could be readily incorporated into Nafion film, the film suffered from slow charge-transfer and long-term stability problems. To overcome these drawbacks, Dong's group developed CNT/Nafion composite films to immobilize $Ru(bpy)_3^{2+}$ on a glassy-carbon (GC) electrode [15]. Because the composite film had more open structures and a larger surface area and because CNTs provided conducting pathways for the electron transfer from $Ru(bpy)_3^{2+}$ sites to the electrode surface, the CNT/$Ru(bpy)_3^{2+}$ composite film could accelerate electron transfer and diffusion of $Ru(bpy)_3^{2+}$. As a result, the solid-state sensor prepared had ECL intensity three orders higher than that of the pure Nafion film-modified electrode in TPrA detection [15].

Ju and co-workers have reported the determination of reduced nicotinamide adenine dinucleotide (NADH) on a CNT/$Ru(bpy)_3^{2+}$ composite film-modified GC electrode. Their results gave sensitivity comparable with others [20].

Lee et al. reported the solid-state ECL from immobilized in titania (TiO_2)-Nafion composite film. They found that ECL of $Ru(bpy)_3^{2+}$ depended on the amount of Nafion incorporated into the composite film and the 50% Nafion content (i.e. volume$_{(the\ as\text{-}prepared\ titania)}$: volume$_{(5\%\ Nafion\ solution\ in\ aliphatic/water)}$ = 1:1) gave the maximum ECL signals in both TPrA and oxalate detection [17].

Simple and sensitive ECL detection of antihistamine chlorphenamine maleate (CPM) was reported by Zhang's group using a TiO_2/Nafion composite film-modified GC electrode [21].

Eastman AQ55D polymer (AQ), a kind of poly(ester sulfonic acid) cation-exchange polymer, is similar to Nafion in that it both contains sulfonated cation-exchange sites and shows strong adherence to the surface and a simple coating procedure. However, AQ has some advantages over Nafion due to its more hydrophilic character, lower cost, more rapid response and anti-fouling properties, so AQ could be readily used as an alternative to Nafion to fabricate solid-state ECL sensors [29–31].

Dong et al. have determined commonly-used depressant chlorpromazine (CPZ) with a linear range of 1–200 μM using a silica/AQ/$Ru(bpy)_3^{2+}$ thin film-modified GC electrode [29].

Wang and co-workers have developed an interesting method for fabricating solid-state ECL sensors using AQ polymer [30]:

Figure 1. Routine for the preparation of PtNPs/AQ/Ru(bpy)$_3^{2+}$ colloid [30].
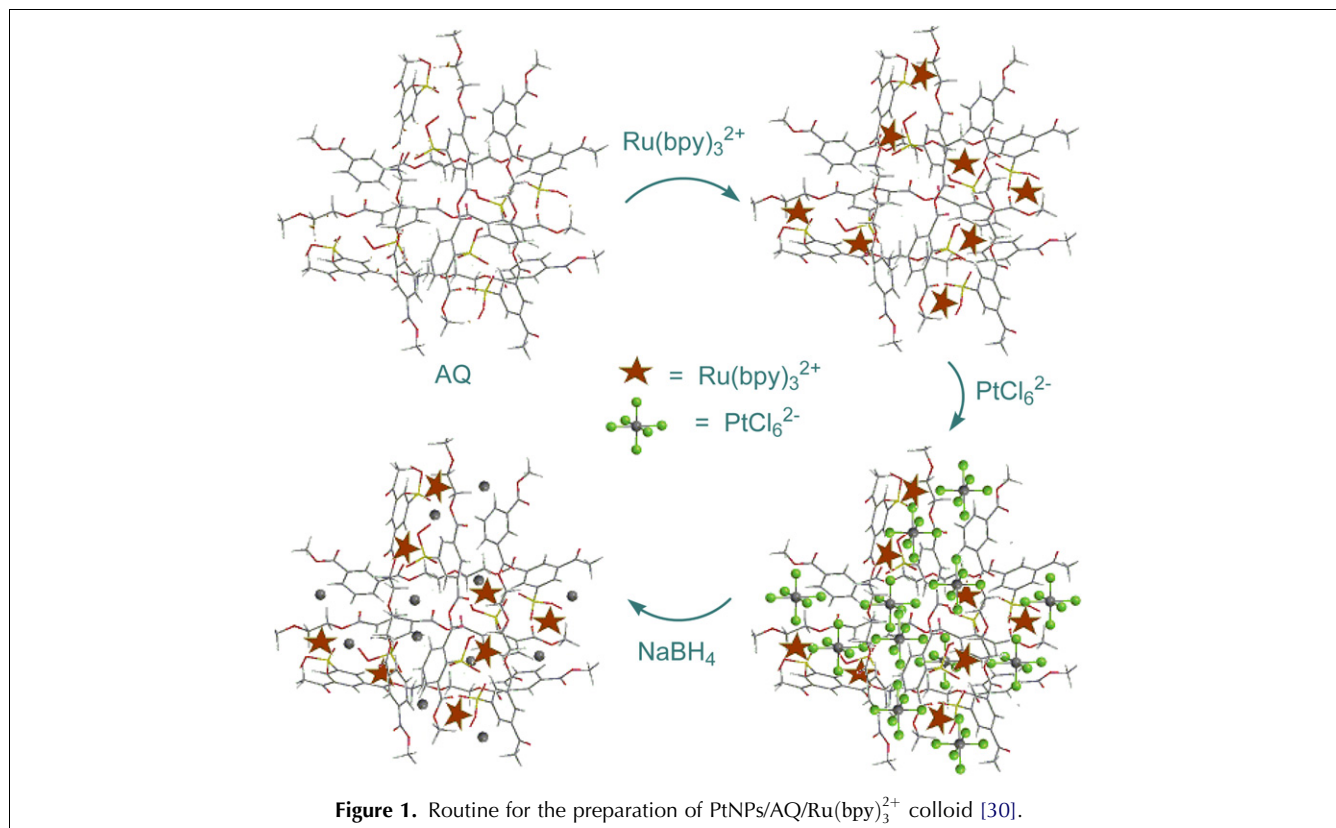
- first, the platinum NP (PtNP)/AQ/Ru(bpy)$_3^{2+}$ colloidal material was synthesized through a wet-chemical routine (Fig. 1.); and,
- then, the colloids prepared were directly coated onto a GC-electrode surface to produce an ECL sensor.
  The AQ played two important roles in the sensor:
- one as the cation exchanger for Ru(bpy)$_3^{2+}$; and,
- the other is the dispersant of the PtNPs.

In TPrA detection, the sensor showed excellent sensitivity, which could be assigned to the combination of PtNP and permselective AQ polymer. A very low limit of detection (LOD) (1 fM) of TPrA was obtained [30].

3.2. Ru(bpy)$_3^{2+}$-infused polymer
The metallopolymer incorporated with Ru(bpy)$_3^{2+}$ has been synthesized and its ECL properties were studied by Dennany and co-workers [32–34]. [Ru(bpy)$_2$(PVP)$_{10}$]$^{2+}$, where PVP is poly(vinylpyridine), has been used to construct a DNA sensor on a basal plane pyrolytic graphite (PG) electrode [32]. The sensor was constructed by layer-by-layer electrostatic assembly of [Ru(bpy)$_2$(PVP)$_{10}$]$^{2+}$ and DNA. Direct ECL was obtained by catalytic oxidation of guanine bases in DNA.

Lu and Whang performed detailed studies on ECL and the electrochemical behavior of an [Ru(bpy)$_2$(PVP)$_{10}$]$^{2+}$/oxalate system on an indium tin oxide (ITO) electrode [35].

Ru(bpy)$_3^{2+}$ can also be covalently attached to silica polymers [36–38]. Lee et al. synthesized a functionalized

Ru(bpy′)$_3^{2+}$ complex where bpy′ is a modified bipyridine ligand with polymerizable trimethyloxysilyl end groups (Fig. 2) [36]. The complex could be spin-coated onto an ITO electrode and then gelatinized to form a porous structure having 50–150-nm nanopores. Several analytes were detected and showed good ECL responses with the Ru(bpy′)$_3^{2+}$ complex gel film-modified ITO electrode. Moreover, the Ru(bpy′)$_3^{2+}$ gel film-coated ITO electrode showed excellent long-term stability and the loss in ECL intensity after storing at room temperature for more than six months was only 10% [36].

Another kind of Ru(bpy)$_2$(bpy″)$^{2+}$ complex covalently embedded into silica polymer was synthesized by Wiles's

The structure of Ru(bpy')₃²⁺Cl₂

Figure 2. Chemical structure of the Ru(bpy′)$_3^{2+}$ complex [36].
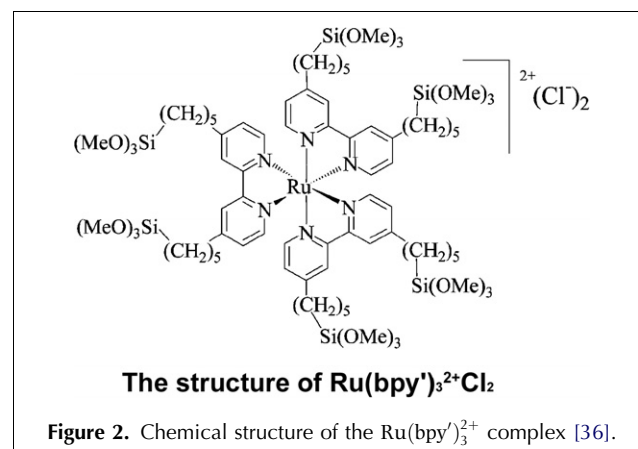
group [37]. The bpy″ ligand was prepared through amidation reaction by covalent attachment of 4,4′-dicarboxy-2,2′-bipyridine to (3-aminopropyl)triethoxysilane. The Ru(bpy)$_2$(bpy″)$^{2+}$ complex was then covalently attached to a silica surface and ECL detection of codein was studied.

Our group synthesized the same Ru(bpy)$_2$(bpy″)$^{2+}$ complex through a similar procedure [38]. The complex then was gelatinized and spin-coated onto an ITO electrode to make a solid-state ECL sensor (Fig. 3). The ITO electrode prepared showed good stability with excellent ECL behavior (Fig. 3).

3.3. Silica sol gel and nanoparticles

Besides the silica-based polymers, silica sol gel and NPs have also been employed to construct solid-state ECL sensors [39–52]. Silica sol-gel materials provide advantages over many polymeric materials (e.g., their porous properties, and the ease with which they can be prepared, modified and doped with various reagents).

Pastore et al. produced an ECL sensor by embedding Ru(bpy)$_3^{2+}$ inside thin films of silica glass [39]. Their sol-gel films were transparent, crack-free and homogeneous reddish layers, having a thickness of 200 ± 20 nm.

Cyclic voltammetry (CV) measurements showed the diffusion-controlled redox behavior of the Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ system (Fig. 4). The sensor prepared had a very fast response in ECL detection of oxalate (less than 100 ms) [39].

Collinson's group investigated the ECL of Ru(bpy)$_3^{2+}$ and its co-reactants entrapped within sol-gel-derived silica monoliths using an immobilized ultramicroelectrode assembly [40]. Their results indicated that solid-state ECL strongly depends on the nature of the entrapped reagents and the physicochemical properties of the matrix. The ECL sensor was found to be stable upon continuous oxidation or upon drying the gels in a high-humidity environment for over 10 days [40].
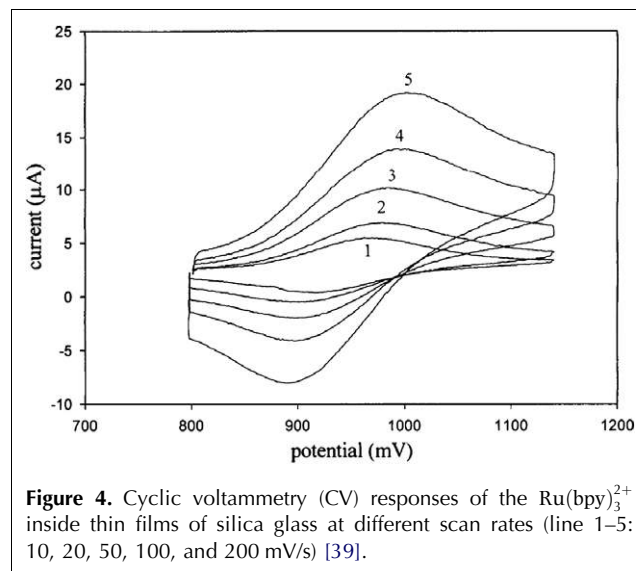
Figure 4. Cyclic voltammetry (CV) responses of the Ru(bpy)$_3^{2+}$ inside thin films of silica glass at different scan rates (line 1–5: 10, 20, 50, 100, and 200 mV/s) [39].

Dong and co-workers developed an ECL sensor based on multilayers of silica NPs/Ru(bpy)$_3^{2+}$ using an electrostatic layer-by-layer method (Fig. 5) [42]. Due to the high surface area and special structure of the silica NPs, the multilayer-film sensor showed high sensitivity and long-term stability. The sensitivity in TPrA detection was more than an order of magnitude greater than that observed for previously reported immobilization methods, and the sensor showed better stability of at least 1 month [22,42].

The same group has reported a novel solid-state ECL sensor using Ru(bpy)$_3^{2+}$-doped silica NPs prepared by a water/oil microemulsion method [50]. The sensor was constructed on a GC electrode through conjugation with a biocompatible chitosan membrane. Their sensor showed high sensitivity and reproducibility in detecting TPrA with an LOD of 2.8 nM.
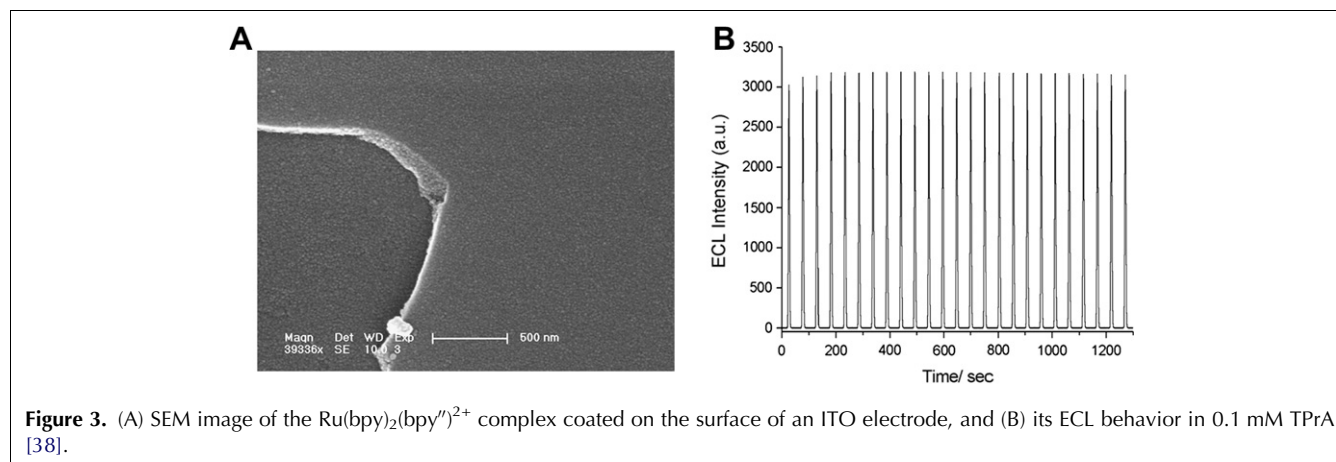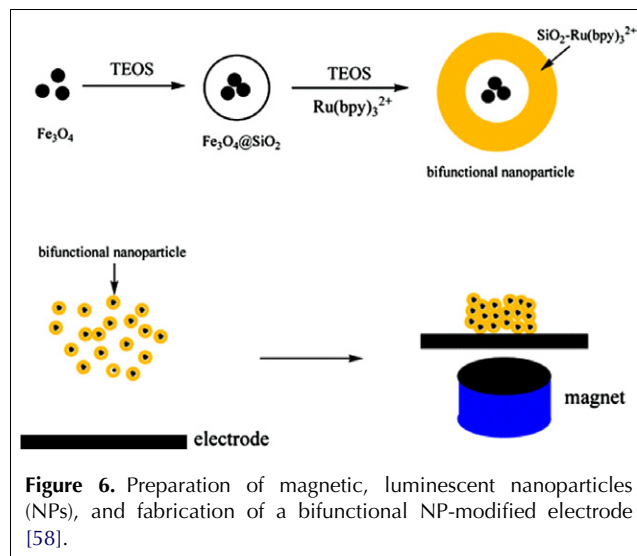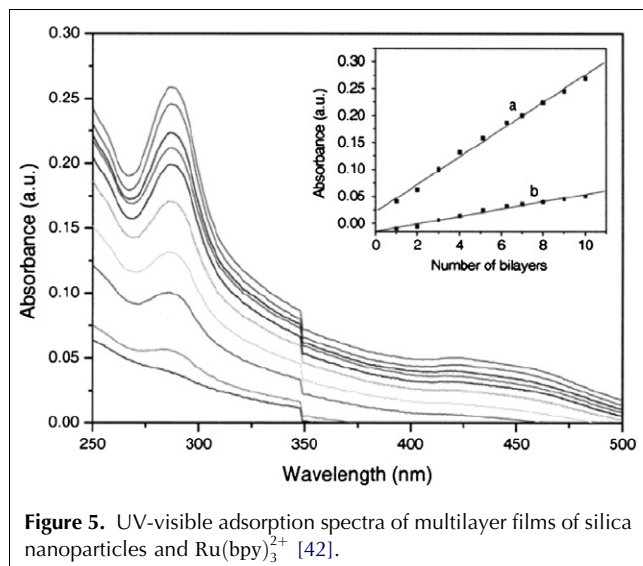
Figure 3. (A) SEM image of the Ru(bpy)$_2$(bpy″)$^{2+}$ complex coated on the surface of an ITO electrode, and (B) its ECL behavior in 0.1 mM TPrA [38].

Figure 5. UV-visible adsorption spectra of multilayer films of silica nanoparticles and Ru(bpy)$_3^{2+}$ [42].

Figure 6. Preparation of magnetic, luminescent nanoparticles (NPs), and fabrication of a bifunctional NP-modified electrode [58].

3.4. Metal nanoparticles

Apart from silica, other nanomaterials have been employed to fabricate solid-state ECL sensors [53–56].

13-nm gold NPs (GNPs) were investigated to immobilize Ru(bpy)$_3^{2+}$ on an ITO electrode [53]. With this method, Ru(bpy)$_3^{2+}$-GNP aggregates were first formed in aqueous medium, then the aggregates formed were cast onto a sulfhydryl-derivated ITO electrode surface via Au-S interaction. An ECL intensity-time curve indicated that the modified electrode was quite stable. PtNPs, synthesized through thermal treatment of a 3-thiophenemalonic acid/H$_2$PtCl$_6$ solution, have also been used to fabricate solid-state ECL sensors [54].

Another kind of solid-state ECL sensor based on GNPs was prepared by Yang's group [55]:

- Ru(bpy)$_3^{2+}$-doped silica NPs were first prepared using the Stöber method;
- the surfaces of the silica NPs were then modified by 3-aminopropyl triethoxysilane (APTES) and negatively-charged GNPs were assembled onto the APTES-modified silica NPs using the strong electrostatic interaction between silica NPs and GNPs; and, finally,
- the silica-GNP-Ru(bpy)$_3^{2+}$ particles were deposited onto the 3-mercaptopropyl trimethoxy silane (MPT-MS) pretreated ITO electrode using Au-S interaction [55].

The ECL sensor showed good reproducibility and stability in TPrA detection.

3.5. Magnetic nanoparticles

Magnetic NPs have also been employed to fabricate Ru(bpy)$_3^{2+}$ ECL sensors [57–59]. Nafion-stabilized magnetic NPs (Nafion/Fe$_3$O$_4$) were synthesized and were then immobilized on a Pt electrode using the magnetic attraction between the Nafion/Fe$_3$O$_4$ NPs and the

magnet behind the Pt electrode surface [57]. Incorporation of Ru(bpy)$_3^{2+}$ into the Nafion/Fe$_3$O$_4$ films was realized via a cation-exchange reaction. Because the Nafion/Fe$_3$O$_4$ films had a greater surface area-to-volume ratio than that of pure Nafion films, the modified electrode had higher mass transport and faster ion-exchange kinetics, so it exhibited more sensitive ECL responses in TPrA detection.

The ECL of Ru(bpy)$_3^{2+}$ immobilized on magnetic microbead surfaces was studied by Oyama et al. [59]. Their results indicated that ECL was affected by the geometrical distribution of the magnetic microbeads on the electrode surface. Moreover, the presence of NaN$_3$ could affect ECL and the mechanism of that effect was studied [59].

Recently Dong and co-workers reported on a solid-state ECL sensor using bifunctional NPs of magnetic core luminescent shell [58]. The surfaces of magnetic iron-oxide NPs were first coated with silica, then an outer shell of Ru(bpy)$_3^{2+}$-doped silica was grown onto the magnetic core using the Stöber method (Fig. 6). The bifunctional NP-cast GC electrode could easily be constructed using an external magnetic field within a few minutes. Using this sensor, detection of TPrA and polyamines spermidine and spermine was more sensitive by two orders of magnitude than the ultraviolet method [58].

3.6. Other materials

Besides all the materials mentioned above, many other materials have also been investigated to develop cost-effective, regenerable solid-state ECL sensors (see Table 1) [60–69].

For example, the ECL of Ru(bpy)$_3^{2+}$ immobilized in clay/Ru(bpy)$_3^{2+}$ multilayer films on an ITO electrode using electrostatic layer-by-layer assembly was investigated [60]. Solid-state ECL was also observed with:

Table 1. Selected papers on solid-state ECL using $Ru(bpy)_3^{2+}$

Electrode	Matrix	Interaction	Analyte	Limit of detection	Ref.
GC	Nafion	Cation ion-exchange	TPrA	1 µM	[14]
			Oxalate	1 µM	
			Alkylamines	10 nM	
			NADH	1 µM	
GC	CNT/Nafion	Electrostatic layer-by-layer assembly	TPrA	10 nM	[15]
GC	CNT/Nafion	Cation ion-exchange	Dopamine	0.6 nM	[16]
			Epinephrine	20 nM	
GC	TiO$_2$/Nafion	Cation ion-exchange	TPrA	1µM	[17]
			Oxalate	1 µM	(HPLC)
			Erythromycin	1 µM	
GC	CNT/TiO$_2$/Nafion	Cation ion-exchange	TPrA	10 nM	[18]
			Oxalate	1 µM	
GC	V$_2$O$_5$/Nafion	Cation ion-exchange	TPrA	10 nM	[19]
GC	CNT/Nafion	Cation ion-exchange	NADH	0.82 µM	[20]
GC	TiO$_2$/Nafion	Cation ion-exchange	CPM	6 ng/mL	[21]
GC	Silica/Nafion	Cation ion-exchange	TPrA	0.1µM	[22]
			Oxalate	2 µM	
Platinum	Nafion	Cation ion-exchange	TMA gas	3 ppb	[23]
GC	ZrO$_2$/Nafion	Cation ion-exchange	Tramadol	25 µM	[24]
			Lidocaine	5 µM	(microchip CE)
			Ofloxacin	10 µM	
Graphite	ZrO$_2$/Nafion	Cation ion-exchange	TPrA	5 nM	[25] (CE)
			Lidocaine	10 nM	
			Proline	5µM	
Platinum	TiO$_2$/Nafion	Cation ion-exchange	Promazine	0.529 µM	[26] (HPLC)
			Chlorpromazine	0.833 µM	
			Triflupromazine	1.64 µM	
			Thioridazine	1.71 µM	
			Trifluoperazine	2.94 µM	
			Erythromycin	1.11 µM	
Graphite oxide	Nafion	Cation ion-exchange	Not reported	Not reported	[27]
GC	Silica/AQ	Cation ion-exchange	TPrA	0.1 µM	[29]
			Oxalate	1 µM	
			CPZ	0.1 µM	
GC	PtNPs/AQ	Cation ion-exchange	TPrA	1 fM	[30]
GC	CNT/AQ	Cation ion-exchange	TPrA	30 pM	[31]
PG	Ru(bpy)$_2$(PVP)$_{10}$	Covalent bonds	DNA	1 damaged base in 1000	[32]
ITO	Ru(bpy)$_2$(PVP)$_{10}$	Covalent bonds	Oxalate	Not reported	[35]
ITO	Organosilicate	Covalent bonds	TPrA	1 µM	[36]
			Tartaric acid	Not reported	
			Ascorbic acid	Not reported	
			NADH	Not reported	
			Tryptophan	Not reported	
			Promazine	Not reported	
			Oxalate	Not reported	
			Quinacrine	Not reported	
			Proline	Not reported	
GC	Silica sol-gel	Covalent bonds	Codeine	Not reported	[37]
ITO	Silica sol-gel	Covalent bonds	TPrA	Not reported	[38]
K-glass	Silica	Physical entrapment	Oxalate	1 µM	[39]
Platinum	Silica sol-gel	Physical entrapment	TPrA	Not reported	[40]
			Oxalate	Not reported	
GC	Humic acid/silica/PVA	Electrostatic interaction	TPrA	0.05 µM	[41]
			Oxalate	0.2 µM	
ITO	SiO$_2$	Cation ion-exchange	TPrA	1 nM	[42]
			Oxalate	20 nM	
GC	PSS/silica	Electrostatic interaction	TPrA	0.1 µM	[44] (FIA)
			Oxalate	0.1 µM	
			NADH	0.5 µM	

Table 1. (*continued*)

Electrode	Matrix	Interaction	Analyte	Limit of detection	Ref.
GC	PSS/silica	Ion-exchange	TPrA	0.1 µM	[45]
ITO	$Ru(bpy)_3^{2+}$-doped silica	Physical entrapment	Denatured DNA	0.126 µg/mL	[46]
			Native DNA	0.252 µg/mL	
GC	$Ru(bpy)_3^{2+}$/Nafion/ Silica sol-gel	Cation ion-exchange	Ethanol	10 µM	[47]
GC	Silica sol-gel/PSS	Ion association	Methamphetamine	0.2 µM	[48]
GC	$Ru(bpy)_3^{2+}$-doped silica/CNT	Physical entrapment	TPrA	2.8 nM	[49]
GC	Silica/chitosan	Physical entrapment	TPrA	2.8 nM	[50]
GC	PSS/chitosan/silica sol gel	Electrostatic interaction	Ethanol	9.3 µM	[51]
ITO	SiO_2/CNT	Physical entrapment	TPrA	0.039 nM	[52]
ITO	GNPs	Electrostatic interaction	TPrA	Not reported	[53]
ITO	PtNPs	Electrostatic interaction	TPrA	Not reported	[54]
ITO	$Ru(bpy)_3^{2+}$-doped silica/GNPs	Physical entrapment	TPrA	50 nM	[55]
ITO	GNPs	Electrostatic interaction	Ethanol	3.3 µM	[56]
Platinum	Fe_3O_4/Nafion	Cation ion-exchange	TPrA	50 nM	[57]
GC	Fe_3O_4/silica	Physical entrapment	TPrA	6.5 nM	[58]
			Spermidine	0.84 µM	
			Spermine	0.33 µM	
ITO	Clay	Electrostatic layer-by-layer assembly	TPrA	20 nM	[60]
			Oxalate	100 nM	
Gold	Clay	Electrostatic interaction	Glucose	0.1 mM	[61]
GC	TiO_2	Physical entrapment	Oxalate	5 µM	[62]
			Proline	4 µM	
CPE	Zeolite Y sieves	Ion-exchange	Heroin	1.1 µM	[63] (FIA)
ITO	$W_{10}O_{32}^{4-}$/$Ru(bpy)_3^{2+}$	Electrostatic interaction	TPrA	Not reported	[64]
CPE	MCM-41/IL	Electrostatic interaction	TPrA	7.2 nM	[65] (FIA)
ITO	None	Spin-coating	Not reported	Not reported	[70]
GC	Benzene sulfonic acid monolayer	Electrostatic interaction	TPrA	1 µM	[71]
GC	PSP/CNT	Electrostatic interaction	TPrA	6 nM	[72]
			DBAE	0.25 µM	
ITO	H_2PtCl_6	Electrostatic interaction	TPrA	Not reported	[73]
ITO	$K_3Fe(CN)_6$	Electrostatic interaction	TPrA	Not reported	[74]
GC	CNT/Nafion	Cation ion-exchange	DNA	Single-base mismatch	[75]
ITO	AQ/silica/CNT	Cation ion-exchange	Proline	2 µM	[76]
			DMBA	Not reported	(microchip CE)
			Ofloxacin	Not reported	
Pt	PSS-silica-(PVA-*g*-PVP)	Electrostatic interaction	TPrA	2 nM	[77]
			Proline	2 µM	(CE)

PSS, Poly(sodium 4-styrene sulfonate); PVA, Poly(vinyl alcohol); PVP, Poly(vinylpyridine).

- $Ru(bpy)_3^{2+}$ entrapped in a vapor-deposited titania sol-gel membrane [62];
- $Ru(bpy)_3^{2+}$ entrapped in supercages of zeolite Y [63];
- multifunctional organic-inorganic multilayer films of $Ru(bpy)_3^{2+}$ and decatungstate [64];
- highly-ordered mesoporous SBA-15 [67]; and,
- $Ru(bpy)_3^{2+}$ monolayers [70,71].

We recently developed a solid-state ECL sensor based on homogeneous partial sulfonation of polystyrene (PSP) with a CNT composite film-modified GC electrode [72]. $Ru(bpy)_3^{2+}$ was entrapped into the PSP using electrostatic interactions between sulfonic acid groups of PSP and $Ru(bpy)_3^{2+}$ cations. The CNT was used as not only a conducting pathway to accelerate the electron transfer but also a proper matrix to immobilize $Ru(bpy)_3^{2+}$ on the electrode by hydrophobic interaction. The sensor therefore exhibited enhanced electrochemi-cal and ECL responses compared with those of pure PSP film, and such a sensor could be used for sensitive determinations of 2-(dibutylamino)ethanol (DBAE) and TPrA (Fig. 7) [72].

Some interesting micro-structures made from $Ru(bpy)_3^{2+}$ and metallic salts (e.g., H_2PtCl_6 and $K_3Fe(CN)_6$) were prepared and their solid-state ECL behavior was studied [73,74]. For example, $Ru(bpy)_3^{2+}$-containing micro-structures could easily be obtained using solution-based self-assembly, carried out by directly mixing H_2PtCl_6 and $Ru(bpy)_3Cl_2$ aqueous solutions at room temperature (Fig. 8) [73]. $Ru(bpy)_3^{2+}$ contained in the micro-structures formed on an ITO electrode exhibited a diffusion-controlled voltammetric feature. Moreover, the $Ru(bpy)_3^{2+}$-containing micro-structures showed excellent ECL behaviors in TPrA detection.
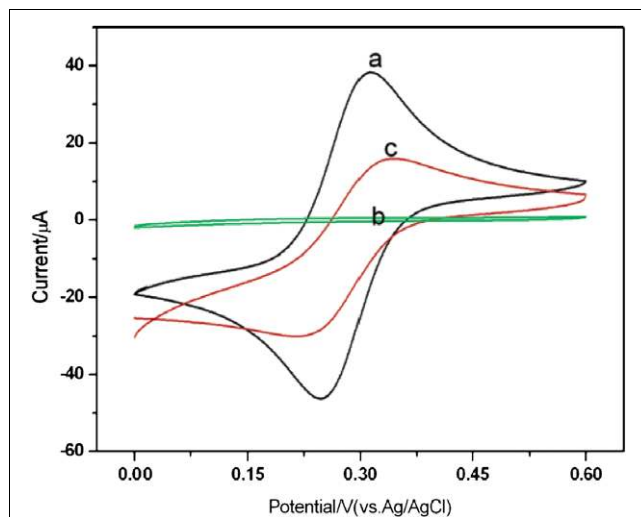
Figure 7. Cyclic voltammetry (CV) responses at (a) bare GC electrode, (b) PSP/Ru GC electrode, and (c) PSP/CNT/Ru GC electrode, respectively, in 5 mM $Fe(CN)_6^{3-}$ in 0.1 M NaCl solution at the scan rate of 50 mV/s [72].
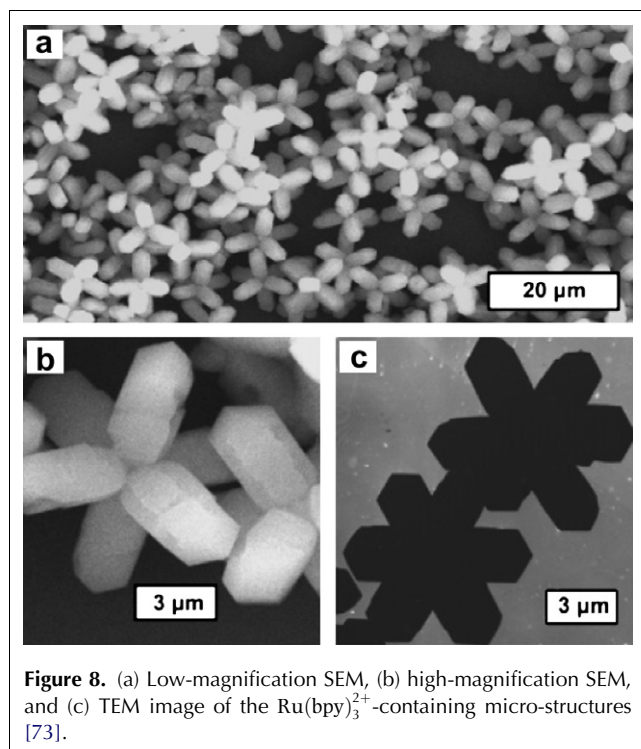

Figure 8. (a) Low-magnification SEM, (b) high-magnification SEM, and (c) TEM image of the $Ru(bpy)_3^{2+}$-containing micro-structures [73].

4. Analytical applications of solid-state ECL of $Ru(bpy)_3^{2+}$

Due to its intrinsic advantages mentioned above and its ease of fabrication, solid-state ECL of $Ru(bpy)_3^{2+}$ shows great promise in analytical applications. Using $Ru(bpy)_3^{2+}$, quite a number of solid-state ECL sensors have been developed for different analytes (e.g., amines,

oxalates, amino acids, drugs, alcohols, glucose and bio-molecules) with low LODs (usually, 1 μM to 1 nM, but can be as low as 1 fM) (see Table 1).

In this section, we focus on analytical applications in stationary solutions of solid-state ECL of $Ru(bpy)_3^{2+}$. We discuss solid-state ECL of $Ru(bpy)_3^{2+}$ coupled to separation techniques in the following section.

4.1. ECL assay of non-biomolecules
Using the mechanisms described above, ECL signals can be used to detect the concentration of co-reactants since the concentration of $Ru(bpy)_3^{2+}$ immobilized on the solid surface is constant. For most cases, TPrA (and/or oxalate sometimes) is usually used as a typical co-reactant to validate the solid-state ECL sensors using $Ru(bpy)_3^{2+}$. Wang and co-workers' results indicated that as little as 1 fM TPrA could be detected using a PtNPs/AQ/$Ru(bpy)_3^{2+}$-modified GC electrode [30].

Lee et al. [36] detected as many as nine analytes (including positively charged, neutral and negatively charged analytes) using their solid-state ECL sensor. Their results indicated that solid-state ECL sensors showed similar responses towards analytes when compared with the ECL responses towards the analytes where the $Ru(bpy)_3^{2+}$ was added in solution.

Usually, solid-state ECL sensors exhibit poor selectivity for multi-analyte detection. However, selectivity could be improved to some extent when ion-exchange films, such as Nafion, were used as the immobilization matrix [14,17,19]. For example, an ECL sensor based on the sol-gel-derived V_2O_5/Nafion composite film-modified GC electrode showed selectivity for positively-charged TPrA over negatively-charged oxalate and ascorbic acid [19]. The sensor also showed a good response to hydrophobic antibiotic erythromycin. Moreover, the ECL sensor did not respond to urea and neurotransmitters, such as dopamine and serotonin, so it could be used for monitoring antibiotics in biological fluids [19].

An interesting trimethylamine (TMA) gas sensor based on $Ru(bpy)_3^{2+}$/Nafion gel has been developed [23]. The sensor exhibited a quick response within 20 s and a linear response to TMA gas in the range 10–310 ppb with an LOD of 3 ppb. More importantly, the sensor could be used to estimate the freshness of practical samples of seafood. The ECL response for squid was almost consistent with a profile curve obtained from the classic measurement of K value (K value being an index of freshness that evaluates the extent of self-digestion of ATP by measuring inosine and hypoxanthine produced in seafood) [23].

4.2. ECL assay of biomolecules
Many biologically important molecules can also be analyzed using solid-state ECL sensors [75]. A glucose sensor based on solid-state ECL using $Ru(bpy)_3^{2+}$-

incorporated clay colloids has been fabricated [61]. Since the excited $Ru(bpy)_3^{2+*}$ could be quenched by oxygen via an energy transfer process, the sensor showed a linear decrease with increasing oxygen pressure. Based on only this effect of oxygen pressure, a glucose sensor was constructed by embedding glucose oxidase (GOx) into the $Ru(bpy)_3^{2+}$/clay colloids [61]. The $Ru(bpy)_3^{2+}$/clay colloids/GOx-modified electrode showed a relative poor performance with a linear range for glucose of 0.1–10 mM at pH 10 [61].

Solid-state ECL sensors of DNA were demonstrated using direct oxidation of guanine (sometimes adenine) bases in DNA by $Ru(bpy)_3^{2+}$. Recently, we reported one-electron catalytic oxidation of guanine bases in DNA using a $Ru(bpy)_3^{2+}$-doped silica NP-modified ITO electrode. The native double-stranded DNA and its denatured counterpart could be discriminated using ECL detection [46].

Dennany and co-workers realized simultaneous direct ECL and electrochemical detection of DNA in ultrathin films [32]. Through their method, chemical damage to DNA caused by styrene oxide could be detected, and the estimated LOD was 1 damaged DNA base in 1000.

Recently, we reported label-free ECL detection of catalytic oxidation of guanine and adenine bases using an $Ru(bpy)_3^{2+}$-modified electrode (Fig. 9) [75]. Native DNA and its thermally denatured counterpart could be distinctly discriminated using ECL detection with a low concentration (3.04×10^{-8} mol/L for Salmon Testes-DNA). Moreover, sensitive single-base mismatch of the p53 gene segment was detected at 39.3 nM [75].

5. Solid-state ECL of $Ru(bpy)_3^{2+}$ coupled to separation techniques

Besides the analytical applications in stationary solution of solid-state ECL of $Ru(bpy)_3^{2+}$, it can also be coupled to separation techniques to overcome poor selectivity. To date, many solid-state ECL electrodes have been widely used as sensitive detectors for flow-injection analysis (FIA), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE) and microchip CE. [3–5,17,24,26,39,44,63,65,76,77]

5.1. Flow-injection analysis (FIA)
FIA was readily coupled with solid-state ECL detectors [39,44,63,65]. To satisfy the demands of FIA detectors, solid-state ECL detectors must be robust in solution. In our laboratory, we fabricated a stable solid-state ECL detector using $Ru(bpy)_3^{2+}$ by immobilizing $Ru(bpy)_3^{2+}$/PSS/silica/Triton X-100 films on a GC electrode [44]. The integrated FIA-ECL system showed good reproducibility for seven consecutive injections of 1 mM oxalate.

Recently, we developed an enhanced solid-state ECL sensor as follows:
- $Ru(bpy)_3^{2+}$ was first incorporated into sulfonic-functionalized MCM–41 silica via electrostatic interaction;
- the $Ru(bpy)_3^{2+}$/MCM − 41 composites were then mixed with graphite particles to construct a carbon paste electrode (CPE) using ionic liquid as a binder [65].

When the ECL sensor prepared was used in FIA for TPrA analysis, it showed good reproducibility and stability (Fig. 10).
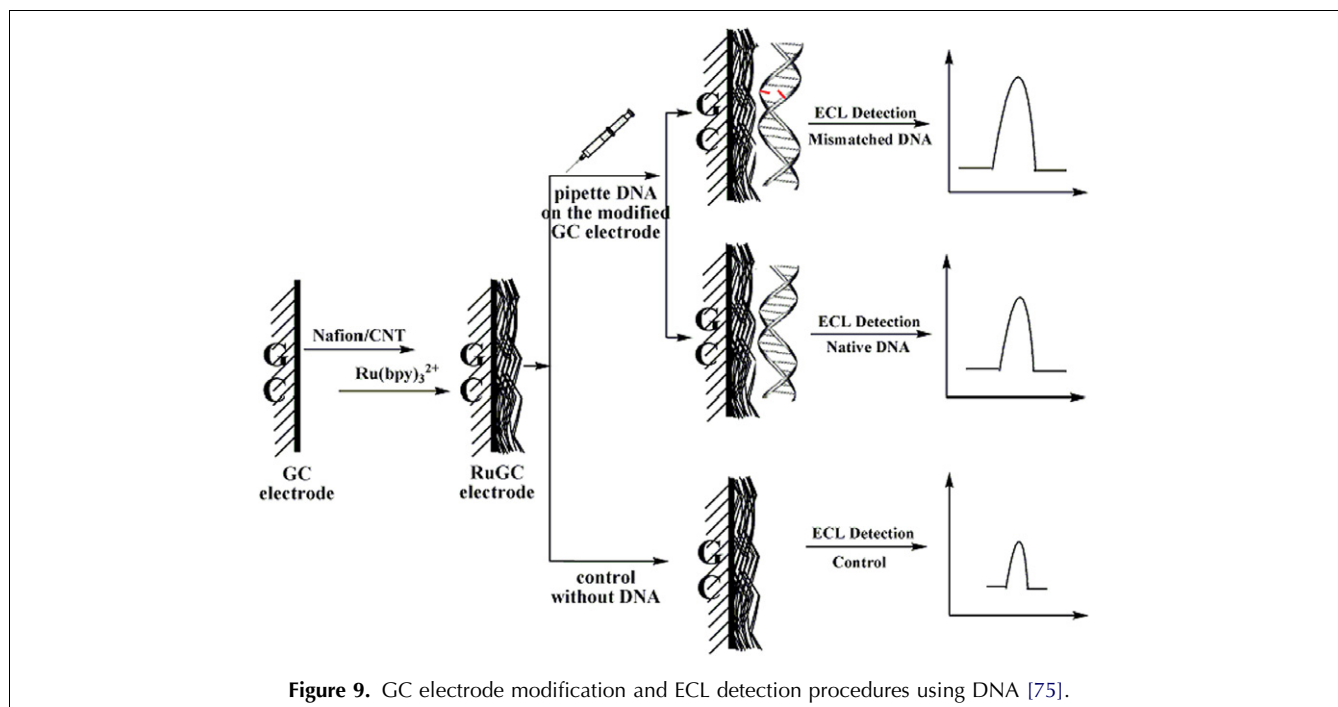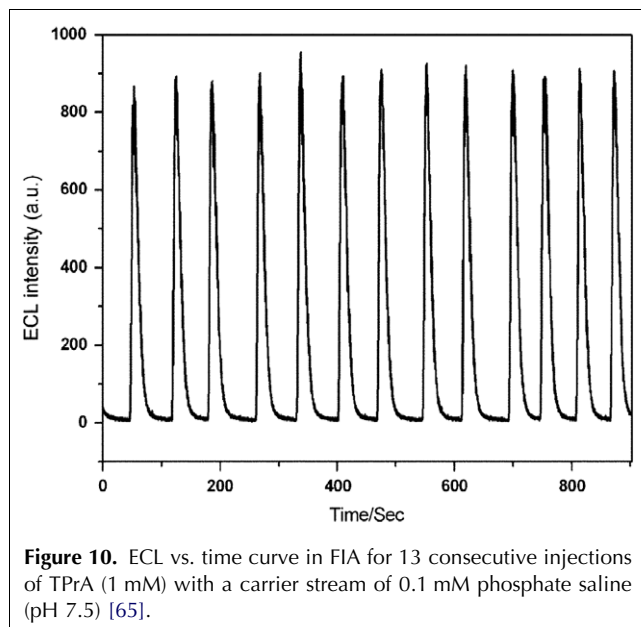

Figure 9. GC electrode modification and ECL detection procedures using DNA [75].

Figure 10. ECL vs. time curve in FIA for 13 consecutive injections of TPrA (1 mM) with a carrier stream of 0.1 mM phosphate saline (pH 7.5) [65].

5.2. High-performance liquid chromatography (HPLC)

In recent years, ECL of $Ru(bpy)_3^{2+}$ has become an attractive detection method for HPLC for a wide range of analytes [3]. In most cases, $Ru(bpy)_3^{2+}$ in solution phase could be introduced into the HPLC system by adding it pre-column to the HPLC mobile phase or post-column to the HPLC effluent [3]. However, these solution-phase methods suffered from band broadening and wasted $Ru(bpy)_3^{2+}$. The use of solid-state ECL detectors can overcome the above flaws [17,26].

Lee's group integrated HPLC with a solid-state ECL detector for the determination of erythromycin in human-urine samples [17]. Their ECL detector was devised by immobilizing $Ru(bpy)_3^{2+}$ in sol-gel-derived TiO_2/Nafion composite films on a GC electrode. The HPLC/solid-state ECL system was quite stable in the mobile phase containing a high content of organic solvent acetonitrile (30%, v/v) over experimental time-scales. The ECL signals of the sensor decreased <10 % over 5 h. By contrast, the ECL signals of a pure Nafion-based sensor decreased <50 % in 1 h under the same experimental conditions [17].
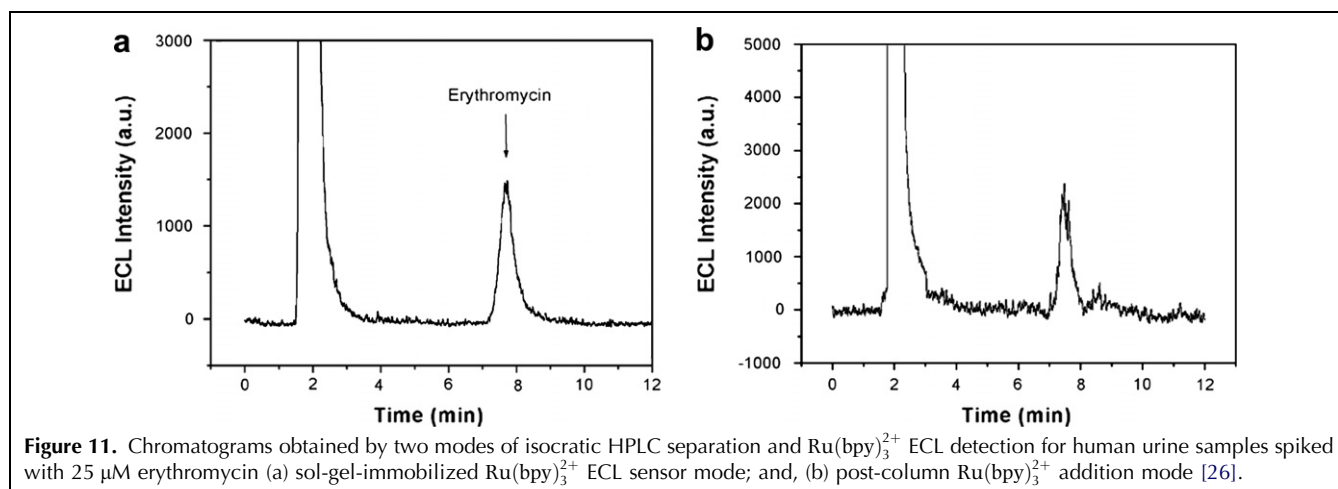
The same group further investigated the difference between HPLC with a solid-state ECL system and HPLC with a conventional system for adding $Ru(bpy)_3^{2+}$ post-column (Fig. 11) [26]. Their results indicated that the analytical performance of the HPLC/solid-state ECL system was no worse than that of the HPLC/system adding $Ru(bpy)_3^{2+}$ post-column.

5.3. Capillary electrophoresis (CE)

Combining the merits of CE (high-efficient separation) and ECL (sensitive detection), CE-ECL techniques have been extensively studied and found many applications in analytical fields [4,5].

Recently, much attention has been paid to CE coupled with solid-state ECL detectors [25,77]. Wang et al. built for the first time a CE-ECL system with a solid-state ECL detector [77]. The detector was fabricated by casting an $Ru(bpy)_3^{2+}$-PSS-silica-(PVA-g-PVP) film on a Pt electrode. The modified Pt electrode displayed good stability in solution (the ECL detector remained stable in the phosphate solution for about 24 h), so it met the requirements of combining with CE. The CE-ECL system was validated through separating and detecting TPrA and proline under optimal conditions [77].

Chen's group [25] has developed a solid-state ECL detector suitable for CE. The detector was constructed by coating sol-gel-derived zirconia (ZrO2)/Nafion films onto a graphite electrode, and $Ru(bpy)_3^{2+}$ was then incorporated into the film using ion-exchange interaction. Under optimal conditions, the CE-ECL system was successfully used to separate and detect TPrA, lidocaine and proline.

Figure 11. Chromatograms obtained by two modes of isocratic HPLC separation and $Ru(bpy)_3^{2+}$ ECL detection for human urine samples spiked with 25 μM erythromycin (a) sol-gel-immobilized $Ru(bpy)_3^{2+}$ ECL sensor mode; and, (b) post-column $Ru(bpy)_3^{2+}$ addition mode [26].

5.4. Microchip CE

Due to its promising advantages (e.g., efficient separation, short analysis time, minute consumption of samples and reagents, and portability), microchip CE has recently received increasing attention in analytical chemistry. However, less attention has been paid to coupling microchip CE with solid-state ECL detectors using $Ru(bpy)_3^{2+}$ [24,76]. The combination of microchip CE and solid-state ECL of $Ru(bpy)_3^{2+}$ would make the separation/detection system more integrated and simpler.

Chen and co-workers have detected pharmaceuticals tramadol, lidocaine and ofloxacin on a CE microchip using a solid-state ECL detector [24].

We have proposed a novel microchip CE coupled to solid-state ECL detection using $Ru(bpy)_3^{2+}$ based on an $Ru(bpy)_3^{2+}$/AQ/silica/CNT composite film-modified ITO electrode (Fig. 12) [76]. The microchip was fabricated with a micro molding in capillary (MIMIC) technique using poly(dimethylsiloxane) (PDMS). Our system displayed relatively good durability and stability in proline detection (the modified electrode had a lifetime of 4 h). Moreover, the system could be used to separate and detect ofloxacin and 4-(dimethylamino)butyric acid (DMBA).
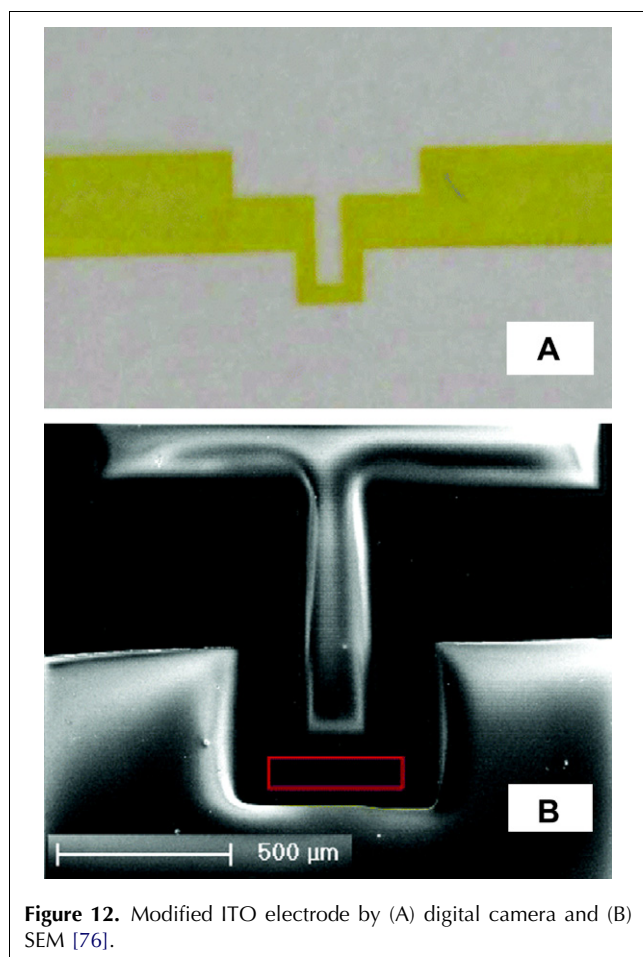

Figure 12. Modified ITO electrode by (A) digital camera and (B) SEM [76].

6. Conclusions and outlook

Compared with solution-phase ECL of $Ru(bpy)_3^{2+}$, solid-state ECL of $Ru(bpy)_3^{2+}$ exhibited several advantages (e.g., reducing consumption of expensive reagent, simplifying experimental design, and enhancing ECL sensitivity). To date, quite a number of methods and materials have been developed to fabricate solid-state ECL sensors using $Ru(bpy)_3^{2+}$. Though much progress has been made to improve sensitivity, robustness and regenerability of solid-state ECL sensors, many new methods and materials are still needed to further improve sensor performance in practical applications [15–77]. Further improvements could be realized by:

(1) immobilizing a large number of $Ru(bpy)_3^{2+}$ molecules on an electrode surface using silica-NP encapsulation, ion-exchange polymers or dendritic molecules containing more than one $Ru(bpy)_3^{2+}$ molecule [1];

(2) improving the conductivity of the composite films immobilized by introducing conductive nanomaterials, such as CNT and metallic NPs [53,54,75]; and,

(3) covalently attaching $Ru(bpy)_3^{2+}$ to polymer to prevent leakage of $Ru(bpy)_3^{2+}$ and improve robustness.

For solution-based ECL, much attention has been paid to improving ECL efficiency by adding additives (e.g., non-ionic surfactants, metal complexes, or halide ions) to the electrolyte [78]. Recently, our group demonstrated that ECL efficiency could be enhanced by introducing ionic liquids [79], so, by introducing some functionalized materials (e.g., nanomaterials and ionic liquids), novel solid-state ECL could be explored in the future. Besides, solid-state ECL using reagents other than $Ru(bpy)_3^{2+}$ should be another interesting and promising research field to explore [80].

Though solid-state ECL sensors using $Ru(bpy)_3^{2+}$ have been coupled with several techniques for separation and detection of a wide range of analytes, very few reports have focused on microchip/solid-state ECL [24,76]. Miniaturized chips exhibit several merits (e.g., short analysis time, low consumption of reactants and ease of automation), so combination the microchip and solid-state ECL sensors using $Ru(bpy)_3^{2+}$ should have great potential in many analytical applications in the future.

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