ECL is one of the leading analytical tools, which is being widely used in a variety of sensing and biosensing applications. In recent years, ECL has become a popular technique in analytical chemistry because of its simplified optical setup, versatility, good spatial temporal control, and more importantly, no background signals. ECL has been extensively studied in various applications, particularly in bioanalysis, and light-emitting devices [LEDs]. Most of the recent studies specifically utilized metal complexes, organic molecules, carbon and metal-based nanomaterials as ECL luminophores. ECL phenomenological studies of metal complexes are mainly for three reasons. At first, tris(2,2'-bipyridine) ruthenium (II) abbreviated as Ru(bpy)_3^2+ has achieved overwhelming success in vitro diagnosis (IVD) because of its wide dynamic range, simplicity, high sensitivity, rapidness and stable labels by coupling with DNA probe assays and immunoassays. Secondly, the ECL of the ruthenium based metal complex allows the direct detection of various co-reactants, which are responsible for a variety of applications. Thirdly, the irridium based metal complexes enable easy color tuning that is attributed to broadening the ECL to LEDs and analytical applications. The data from the web of science shows that since from first discovery of ECL by Hercules, almost 9646 ECL articles have been reported. The previous reports pointed out that about 4700 ECL articles were published during 1960–2005. The numerical difference have been evidence of how fast the ECL is developing in recent years.

Luminophore is the heart of ECL, it should be electroactive and luminescent. So far, three different categories of luminophores have been established such as inorganic metal complexes, organic molecules, and nanomaterials. The complexes or clusters containing materials like, ruthenium (Ru), osmium (Os), copper (Cu), silver (Ag), platinum (Pt), iridium (Ir), gold (Au), and rhenium (Re) comes under inorganic systems. Among these, Ru(bpy)_3^2+ is the most popular and widely used classical luminophore in the majority of the ECL studies. The characteristic advantages of Ru(bpy)_3^2+ luminophore is its ability to be soluble in both aqueous and non-aqueous solvents, high quantum efficiency, stable electrochemical redox response in aqueous and organic electrolytes, and stable chemical stability. Further, it can be utilized as a model luminophore in various ECL systems. Later, the osmium (Os) polypryidine complexes have shown excellent ECL behavior as a luminophore. The Os-based complexes are more photostable and they possess less oxidation potentials over the Ru-based complexes, hence Os-complexes have been used in DNA analysis. Because of their high spin–orbit coupling, the Os-complexes have low intense ECL emission with less lifetime. This feature limits their applicability in recent ECL studies. Orthometalated Ir(III) complexes have also shown their contribution as potential luminophores. It has less redox potentials, as like Ru-complexes and exhibits strong emission in organic medium. The first ECL study was established in organic systems, which are aromatic hydrocarbons (anthracene and rubrene). After that, several organic systems were discovered as luminophores, such as acridinium esters, chrysene, lucigenin, luciferace, pyrene, and luminol etc. Luminol and its derivatives have been designated as the classical organic luminophore as they are playing vital role in ECL phenomenon as a luminophore after Ru(bpy)_3^2+. ECL of luminol appears at very less oxidation potentials, hence it can be used for low potential operation (LPO) ECL studies. LPO ECL has many advantages over high potential operation (HPO) ECL, because at higher oxidation or reduction potentials it will leads to damage in biosensor coatings and biological probes. Hence, ECL of luminol has more advantages over other organic luminophores. Nanomaterials such as quantum dots (QDs), metal clusters are frequently used as ECL reagents. Metal based QDs like cadmium selenide (CdSe), cadmium sulfide (CdS), cadmium telluride (CdTe), cadmium selenide sulfide (ZnS), and CdZnSe, and carbon-based QDs such as carbon QDs (CQDs) and graphene QDs (GQDs) are the mostly used nanomaterials as luminophores. One of the major advantages of these nanomaterials is that they can easily make covalent linkage with other molecules.
which leads to enhancement in the ECL intensity. For example, the covalently linked nitrogen-doped CQDs (N-CQDs) with Ru(bpy)₃²⁺ shows remarkable and enhanced ECL intensity in aqueous electrolytes. Also, N, N-diethylethylenediamine (DEDA) linked with gold nanoclusters shows strong ECL signal in blank electrolytic solution. Moreover, ECL can be utilized for the detection of small molecules like DNA,⁵³ immunoassays,⁵⁶,⁵⁷ aptamers,⁴⁹,⁵⁸,⁵⁹ cancer cells,⁶⁰ pollutants and metal ions.⁶¹ The conventional ECL can be further modified to develop commercialized devices for biosensor applications. For example, wireless,⁶² bipolar electrode-based ECL,⁶³ FIA-ECL,⁶⁴ capillary electrophoresis-based ECL,⁶⁵ and SECM-coupled ECL.⁶⁶ However, the FIA-ECL systems shows much attention in ECL than other ECL-coupled techniques due to its high sensitivity, simplicity, opacity, easy to handle, and wide dynamic range.⁶⁶ Even though FIA-ECL has tremendous application, still it requires further developments for futuristic applications. To the best of our knowledge, there is no review on FIA-ECL based biosensors. This critical review discusses the vibrant developments in FIA-ECL, mechanism of ECL, design of FIA-ECL, and highlights the application of FIA-ECL for the detection of immunoassays, catecholamines, antioxidant compounds, choline, tetracyclines, and pharmaceutical drugs. The current review will pave the way for the design and development of FIA-ECL for efficient point of care applications.

ECL Mechanism

In ECL, the emission of light by luminophore molecule could follows two different kinds of mechanism named as annihilation and co-reactant mechanism. In the case of annihilation mechanism, the luminophore molecule alone participates to emit light. Initially the luminophore molecule get oxidizes during the oxidation potential scan and produces cationic intermediate, and then generates anionic intermediates during the reduction potential scan and vice versa. The energetic transfer of electrons between the cationic and anionic intermediates leads to the production of an excited and ground state molecule. Finally, the excited luminophore molecule emits the light during its journey to the ground state. The emission of light by rubrene molecule in acetonitrile follows annihilation mechanism. As shown in Fig. 1, rubrene molecule produces cationic and anionic rubrene intermediates during the anode to cathode potential scan directions. Then an energetic electron transfer occurs from anionic to cationic rubrene intermediate, which in turn produces excited state of rubrene, then emits light.

The annihilation ECL mechanism has some limitations, at first it requires wide range potential window to produce light emission, and hence this mechanism is possible only in organic electrolytes. Because of gas evolution reactions at higher potentials, this mechanism cannot occur in aqueous medium. These factors limit it’s the applications of ECL in aqueous systems. The alternate ECL mechanism named as co-reactant mechanism developed by A.J. Bard in order to overcome the limitations caused in the annihilation mechanism.⁶⁸ The co-reactant ECL strategy carried out by luminophore along with an additional species is called as a co-reactant molecule. The co-reactant mechanism happens in both aqueous and nonaqueous electrolytes and it can be operated exclusively at either anode or cathode direction. Based on the potential scan directions the co-reactant ECL is classified into two different types named as oxidative-reduction mechanism and reductive-oxidation mechanism. ECL of Ru(bpy)₃²⁺/tripropylamine (TPrA) is the first developed co-reactant ECL system and which is a classic example of oxidative-reduction mechanism.⁶⁹ As can be seen in Fig. 2, Ru(bpy)₃²⁺ molecule get oxidize at anode to produce Ru(bpy)₃³⁺ molecule at the same time TPrA also generates TPA upon oxidation. Then TPA chemically reduces the Ru(bpy)₃³⁺ and generates excited state of Ru(bpy)₂²⁺ which emits light during its journey to the ground state. The overall mechanism involving only at anode and requires a narrow potential window. Other than TPrA, there have been plenty of co-reactants, which have been used widely in oxidative-reduction ECL systems such as oxalates (C₂O₄²⁻),⁷⁰ triethyl amine (TEA),⁷¹ diethyl amine (DEA), ascorbic acid,⁷² dopamine,⁷³ nicotinamide adenine dinucleotide (NADH),⁷⁴ and Dibutylethanolamine (DBAE) etc.⁷⁵ Among these TPrA have been used as a benchmark co-reactant to study the oxidative-reduction ECL reactions. Other hand, the reductive-oxidation ECL reaction occurs exclusively during the cathodic potential scan direction. The co-reactant which is to be reduced on electrode produces anionic reactive radicals which has...
capability to oxidize the luminophore reactive intermediate to excited state. The first ECL based on reductive-oxidation mechanism reported by Bard et al. where potassium persulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) was used as co-reactant and Ru(bpy)\textsuperscript{3+/4+} acts as a luminophore.\textsuperscript{76}

Figure 3 indicates the schematic diagram of reductive-oxidation mechanism involving in Ru(bpy)\textsuperscript{3+/4+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−} system in aqueous medium during the cathode scan potentials. As can be seen in Fig. 3, Ru(bpy)\textsuperscript{3+/4+} molecule reduced at electrode to forms Ru(bpy)\textsuperscript{3+} at the same time the co-reactant (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−}) also reduces to form SO\textsubscript{4}\textsuperscript{2−} and then an energetic electron transfer occurs between these two intermediates to generates an excited Ru(bpy)\textsuperscript{3+} and then emits light. The hydrogen evolution reactions occur prior to the Ru(bpy)\textsuperscript{3+} redox response which prevents the stability of reactive intermediates and suppress the ECL reactions, hence the reductive-oxidation ECL is quite complicated over the oxidative-reduction ECL reactions. So far, hydrogen peroxide, and S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−} are the only co-reactants used to study the reductive-oxidation ECL. One of the works by our group proved that in the presence of partial dissolved oxygen in aqueous electrolytes, glutathione (GSH and GSSG) also acts as co-reactant in cathode ECL.\textsuperscript{3} To overcome the evolution problems, Ru(bpy)\textsuperscript{3+/4+} was replaced with metal based QDs such as CdSe, CdS, CdTe, CdSe/ZnS, and CdZnSe.\textsuperscript{77,79} The carbon-based QDs like GQDs, and CQDs are also paying their contribution as a luminophores in ECL reactions. Apart from these metal clusters, the semiconducting materials like titanium dioxide (TiO\textsubscript{2}) based materials are also acting as cathodic ECL luminophores.\textsuperscript{60}

**Flow Injection Analysis Based ECL Design**

The FIA technique is a kind of dynamic analytical tool which is offering its applications in environmental, food, and pharmaceutical analysis.\textsuperscript{51} Recently construction of ECL coupled with other analytical techniques such as SECM, FIA, and capillary electrophoresis are showing impressive glance. Among those FIA-ECL is one of the hot topics, owing to its variety of applications including immunosensors, antioxidant compounds, biological molecules detection, and metal ion sensors.\textsuperscript{38,82–84} Hence, the construction of such dynamic FIA-ECL technique for the purpose of biosensors is to be an important task. Figure 4 shows the conventional FIA schematic representation, consisting of different compartments such as reagent, carrier, pump, sample valve, reaction coil, detector, and waste.

The pump helps to propel the carrier solution and reagent stream (injected analyze sample), hence it is called as propelling unit, the most commonly used propelling unit is peristaltic pump. The propelling unit consists of a set of rollers that are connected to the rotating drum. The sample tubing is fitted in between the rollers and fixed plate. The flow rate is monitored by inner diameter of sample tube and drum speed. The reagent and carrier solutions are mixed in reaction coil. The commonly used conventional flow cell for ECL studies is schematically depicted in Fig. 5. The detector used in FIA-ECL is a photomultiplier tube (PMT) which plays major role in detecting the light emitted on the electrode surface. PMT is a kind of vacuum tube that consists of four important parts such as photocathode, focusing electrodes, electron multiplier, and anode. The each part of the PMT functions in different way to convert the light into the electrical signal. At first, the passage of light is initiated through the input window. Secondly, the light flux converts into the electron flux in the photocathode compartment. Further, the converted electron flux focused and accelerated by focusing electrodes. The electron flux multiplied into secondary electrons, which are finally collected by the anode materials and send to output meter. The electrochemical cell is placed on the top of the detector and working electrode (WE) should be close to the detector (Fig. 5A).

The conventional FIA-ECL set up contains a thin layer flow cell and PMT which is placed down of the cell (near to the WE). The inlet or outlet which is made with stainless steel serves as counter electrode (CE) and the reference electrode (RE) was placed near to the outlet of the solution. The WE was located in thin layer solution (electrolyte pass through the WE) (Fig. 5A). The similar flow cell set up also used for flat electrodes as shown in Fig. 5B. The disadvantages of conventional ECL systems are as follows. The location of RE at downstream of the solution responsible for the large IR drop and high over flow of potential that attributed to decrease in ECL detection sensitivity. Secondly, there will be much noise in ECL signals due to the high flow resistance. Chi et al.\textsuperscript{85}

![Figure 3. Schematic illustration of reductive-oxidation ECL mechanism involving in Ru(bpy)\textsuperscript{3+/4+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−} system.\textsuperscript{76}](image-url):

![Figure 4. The schematic of flow injection analysis cell design representation.\textsuperscript{51}](image-url)
constructed the new type of FIA-ECL system in order to overcome the aforementioned problems. The schematic diagram of a new type thin-layer flow cell set up is shown in Fig. 6A.

The new type of thin-layer FIA-ECL system consists of a capillary inlet, RE, WE, outlet made with stainless steel which also acts as CE. The electrolyte (buffer solution) is filled with quartz cup which consists of three-electrode set up for ECL and electrochemical analysis and the bottom part of the quartz cup will be used as optical window (Fig. 6A). In ECL, the CE reaction also causes some emission which can be avoided. In the new type of FIA-ECL system the CE outlet is made with stainless steel covered with a plastic jacket to prevent the ECL emission from CE reaction. Pt ring electrode used as WE, the Pt ring is coated at one end of the capillary and then the outer layer of Pt wire is coated with epoxy resin insulator except near to the outlet area. The capillary along with Pt wire is inserted into the quartz cup which contains buffer solution until its tip reaches close to the bottom of the quartz cup. Then the compound capillary shaken to form a thin-layer solution between the tip of the compound capillary and bottom of the quartz cup. As formed thin layer at tip of the compound capillary is shown in Fig. 6B. The thickness of the thin-layer solution should not be more than 50 μm. Finally, the FIA-ECL set up was used for ECL analysis to detect analyte molecule.

Applications of FIA-ECL Based Technique

The luminol and Ru(bpy)$_3^{2+}$ have been used as a luminophores in most of the FIA-ECL studies, because of the high ECL quantum efficiency, chemical and thermal stability over than other luminophores. Further, the modification of electrode with these molecules by chemical or electrochemical methods is simple and they are highly stable on the electrode surface. One of the advantages of these luminophore is that number of derivatives synthesized by chemical and electrochemical methods shows remarkable ECL behavior. Also, the interactions of target biomolecules with luminol and Ru(bpy)$_3^{2+}$ leads to sensitive and selective detection with in the dynamic linear range. The FIA-ECL systems especially used to
Immunoassays, catecholamines, antioxidants compounds, choline, tetracyclines, and pharmaceutical drugs (Scheme 1).

**Imunoassay biosensor.**—The luminol ECL with FIA is used for the immunodetection of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). Two different kinds of strategies such as peroxidase label format, and luminol label format were developed for immunoassay detection of 2,4-D. Linear range was obtained from 0.2 μg l⁻¹ to 200 mg l⁻¹ in the case of peroxidase label format, whereas 0.2 μg l⁻¹ to 200 μg l⁻¹ was observed in the case of luminol label format. In both the cases 2,4-D modified glassy carbon electrode used to fabricate peroxidase label and luminol label formats as shown in Fig. 7A. The peroxidase label format immunoassay is developed as follows. At first the antigen-immobilized electrode is incubated in different dilutions of anti-2,4-D antibodies containing PBS. Then the peroxidase labelled secondary antibodies diluted with 1:100 ratio of PBS containing 0.15% bovine serum albumin (BSA) was coated on the electrode. After that, electrode was washed with PBS and used for FIA-ECL analysis (Fig. 7A).

The antibodies luminol labelling has prepared by drop wise addition of 0.02% glutaraldehyde containing PBS into the solution of 1.65 mM luminol, 0.5 mg ml⁻¹ and polyclonal anti-2,4-D IgG antibodies and then incubated at room temperature for about 30 min. The unreacted luminol and glutaraldehyde is removed by using Sephadex G-25 column. Further to minimize the cross-linking between antibodies, the antibodies containing fractions were diluted in PBS and 0.15% of BSA in 1:2 ratio. Then luminol labeled antibodies introduced on electrode and used for FIA-ECL analysis. After the reaction the electrode in both the formats is regenerated by sonication in 0.1 N HCl about 7 min. To obtain the high signal to noise ratio (S/N) for ECL, the oxidation potential of luminol is optimized. ECL was studied at different applied potentials in the range of +200 to +650 mV under flow stream containing 100 μM of H₂O₂. The oxidation potential of +650 mV shows the maximum S/N ratio, but to avoid the electrode fouling +500 mV of applied potential (S/N is 96%) is used for immunosensor detection. Further the luminol FIA-ECL detection was studied at various H₂O₂ concentration to gain the limit of detection (LOD) and dynamic linear range. The higher linear range was obtained from 5.5 fmoL to 55 nmoL at 600 μM of H₂O₂ concentration. Finally, the adopted FIA-ECL methodology is used for immunodetection of herbicide 2,4-D. The obtained LOD and linear range is same as that observed with horseradish peroxidase label.

Arai et al. developed FIA-ECL method for the detection of human immunoglobulin G (hIgG) using N-(aminobutyl)-N-ethyl isoluminol (ABEI)-labeled anti-hIgG. In this method ABEI is used as luminophore with H₂O₂ as a co-reactant. The effect of pH also studied for better ECL intensity gain, and the electrolyte with pH of 7.8 shows high ECL intensity. Hence this pH of electrolyte was used for immuno sensor analysis. The FIA-ECL system contains carbon fiber as WE, saturated calomel electrode and Pt wire serves as RE and CE respectively. The solution of PBS with H₂O₂ serves as carrier solution. The samples of ABEI-labeled anti-hIgG, and ABEI-labeled anti-hlgG-hIgG are spiked through the sample injector. The ECL experiments are recorded at various amount of antibodies injection and the calibration curve is used to detect the LOD (Fig. 7B). In this case the LOD of hIgG is 80 pg ml⁻¹ in the 1.3 ng ml⁻¹ dynamic range.

**Catecholamine’s detection.**—The dopamine and noradrenaline come under catecholamine family, and these are the chemical neurotransmitters. Dopamine is one of the Parkinson’s disease-causing reagents and plays an important role in venal, cardiovascular, and central nervous systems. Several kinds of spectrometric...
techniques have been used for the detection of dopamine. These include chemiluminescence (CL), coulometry, amperometry, fluorometry and ECL. Among these, ECL-based technique shows more sensitive and selective detection of dopamine at trace level. For example the luminol ECL is used to detect the trace amount of dopamine by FIA-ECL inhibition method.8 The ECL intensity of luminol in aqueous alkaline electrolyte containing dissolved oxygen continuously inhibited during the spiking of small amount of dopamine into the electrolyte solution. The decrease in ECL intensity of luminol is due to the interaction between dopamine and excited state of luminol. The inhibition is due to the chemical reaction between the superoxide radical which is formed by electro-reduction of dissolved oxygen and dopamine molecule. This interaction leads to decrease in the formation of superoxide radicals, probably the ECL intensity of luminol gets reduced. The electrode oxidation potential also plays major role in inhibiting the ECL intensity. The applied potential increases from $+200$ to $+1200$ mV, the ECL inhibition ($\Delta I$) increases up to $700$ mV shows maximum ECL inhibition, further it decreases. The flow rate of the flow cell also influences the $\Delta I$, when the flow rate increases, $\Delta I$ also increases and the highest $\Delta I$ is observed for flow rate of $3$ ml min$^{-1}$.8 The proposed FIA-ECL method detects the dopamine in the range of $5.0 \times 10^{-8}$ to $1 \times 10^{-5}$ M with LOD of $30$ nM and the signal to noise ratio is $3$.

In another study, FIA-ECL of Ru(bpy)$_2^{2+}$/TPrA and Ru(phen)$_2^{2+}$/TPrA systems have been used for the sensitive and selective detection of noradrenaline and dopamine in aqueous solutions.89 Ru complexes and the co-reactants were pumped together with PBS through the carrier solution and the analyte molecule is injected from the injector and recorded the ECL intensity versus time transients for quantitative analysis of analyte. $\Delta I$ is calculated between the ECL intensity before and after injection of analyte ($I_0-I_1$) which is used for the determination of analyte by ECL inhibition strategy. Figure 8A represents the ECL inhibition curves of Ru(bpy)$_3^{2+}$/TPrA system recorded in the presence of $1 \mu$M of noradrenaline (a) and dopamine (b). The ECL inhibition is more in the case of noradrenaline than dopamine which is due to the additional $-\text{OH}$ group presents on the noradrenaline. Further the ECL inhibition increases during the changing of flow rate and obtain maximum at $2.5$ ml min$^{-1}$. The electrode potential is also playing an important role in the ECL inhibition. There are two ECL peaks obtained at $900$ mV and $1050$ mV for Ru(bpy)$_3^{2+}$/TPrA system which is due to direct oxidation of TPrA and electro-oxidation of Ru(bpy)$_2^{2+}$, respectively. But in the case of Ru(phen)$_2^{2+}$/TPrA the ECL is observed at $1010$ mV and $1250$ mV, the peak at $1250$ mV is unknown. The maximum ECL inhibition occurs at $1.05$ V for noradrenaline and dopamine (Fig. 8B). The quenching of ECL intensity of Ru(phen)$_2^{2+}$/TPrA and Ru(bpy)$_2^{2+}$/TPrA systems in the presence of noradrenaline and dopamine is due to the limiting of generation of excited luminophore molecules in the presence of analyte. Under the optimized FIA-ECL conditions, using the Ru(bpy)$_2^{2+}$/TPrA system noradrenaline detected in the linear range of $4 \times 10^{-8}$ to $1 \times 10^{-5}$ mol l$^{-1}$ with the LOD of $2.5 \times 10^{-8}$ mol l$^{-1}$ (S/N = 3). Linear range of $2 \times 10^{-8}$ to $2 \times 10^{-7}$ mol l$^{-1}$ with LOD of $7.1 \times 10^{-8}$ mol l$^{-1}$ is obtained for Ru(phen)$_2^{2+}$/TPrA system. The dopamine molecule is detected by ECL inhibition using Ru(bpy)$_2^{2+}$/TPrA system in the linear range of $8 \times 10^{-8}$ to $2 \times 10^{-7}$ mol l$^{-1}$ with LOD of $5.2 \times 10^{-8}$ mol l$^{-1}$ and the linear range of $4 \times 10^{-8}$ to $2 \times 10^{-7}$ mol l$^{-1}$ with $1.5 \times 10^{-8}$ mol l$^{-1}$ of LOD is obtained for Ru(phen)$_2^{2+}$/TPrA system.89 The adopted FIA-ECL method for dopamine and noradrenaline detection by ECL inhibition strategy is comparable with literature and the linear dynamic range is one or two orders of magnitude wider over the other techniques.

**Determination of antioxidant compounds.**—The role of antioxidants in biological systems is very important to control the damage of enzymatic and nonenzymatic natures. In biological systems the reactive oxygen species (ROS) like H$_2$O$_2$ and O$_2^-$ generated during the metabolism process may lead to cancer related diseases. The biological molecules such as glutathione (GSH), ascorbic acid, lipoic acid, bilirubin, and albumin are the known antioxidants. FIA-ECL is used to detect the ascorbic acid, gallic acid, resveratrol, oligoproanthocyanidin (OPC), and pyrogallol. Xiuhua et al. developed microemulsion-enhanced FIA-ECL method to determine antioxidant compounds.89 In this method, the ECL of luminol/H$_2$O$_2$ system is used as a ECL probe in detecting the antioxidants by FIA-ECL analysis.

The microemulsion cetyltrimethylammonium bromide/n-butanol/n-heptane (CTAB/Buta/Hep/H$_2$O) is prepared by using mixed solutions of CTAB, Buta and n-heptane in the desired amounts and then titrated with PBS at 70 °C. FIA-ECL is conducted by pumping luminol and H$_2$O$_2$ solutions through the carrier compartment, the microemulsion was pumped from the sample injector. The pulse-based voltammetry curves were used to record the ECL signals.
of luminol/H$_2$O$_2$ system. The CTAB plays very important role in surfactant medium to enhance the ECL of luminol molecule. The enhancement in the ECL is due to the formation of an attractive electrostatic attraction between CTA$^+$ and luminol anion (L$^-$) which made generation of a greater number of L$^-$ molecules in neutral and acidic electrolytes and enhances the ECL intensity. As seen in Fig. 9, the droplets of emulsion contains more number of luminol molecules due to the high surface area of emulsion. The existent of co-surfactant and oil, the surface area of microemulsion is higher than micelles. The huge number of luminol molecules which are adsorbed on microemulsions are diffuses to the electrode surface and get oxidized to form anions of luminol (Fig. 9). At the same time H$_2$O$_2$ produces O$_2^{--}$ at upper limiting potentials and OH$^-$ will be generated at lower limiting potentials (Fig. 9). During the Haber-Weiss process singlet oxygen is formed and energy transfer occurs between oxidized luminol and singlet oxygen to produce excited luminophore molecule which emits light (Fig. 9).

The optimized ECL condition of luminol/H$_2$O$_2$ system is used to determine the antioxidant activity of ascorbic acid, resveratrol, OPC, and gallic acid. The ECL intensity of luminol/H$_2$O$_2$ system ($C_{\text{luminol}} = 0.1$ mM, $C_{\text{H}_2\text{O}_2} = 0.1$ mM, pH = 7) is quenched by addition of OPC concentration in the dynamic range of 4.0 to 50 mg l$^{-1}$ and the obtained LOD was 1.12 mg l$^{-1}$ (S/N = 3). Further the real sample analysis was carried out by taking fresh grape skin as analtye, the three test samples shows recoveries in the range of 96.5 to 102.1%, suggesting that the FIA-ECL method effectively detects the OPC in the real samples. Further, the proposed FIA-ECL method was used to test the antioxidant behavior of other antioxidants such as ascorbic acid, gallic acid, and resveratrol. Sun et al. used luminol’s ECL to detect the pyrogallol by using FIA-ECL method, this method enhances the ECL intensity of luminol rather than quenching like previous discussed method. In this approach, KCl and luminol solutions were pumped in the mixing valve with 3.5 ml min$^{-1}$ of flow rate and then the solution was mixed with carrier water and the mixed stream was pumped to the ECL cell. The pyrogallol (100 $\mu$l) was injected into the carrier solution through the injector. The change in the ECL intensity during the pyrogallol addition is calculated by using $\Delta I = I_s - I_b$, where $I_s$ is sample ECL intensity and $I_b$ is blank ECL intensity. This FIA-ECL method is very sensitive to detect the pyrogallol in the range of 0.7 nM to 10 mM with LOD of 16 nM. The interference data shows that the adopted method selectively detects the pyrogallol in the presence of other interfering antioxidants.

**Choline detection.**—Choline is one of the essential and water-soluble nutrients that plays an important role in maintaining the metabolism functions as well as central nervous system. Choline is a base material in constructing the various membranes, lipoprotein phospholipids and neurotransmitter acetylcholine. Choline is presents in various parts of organisms such as liver, kidney, lungs, muscles, and placenta. Its deficiency results in enhancing the deposition of fat contents in liver, and also creates poor muscle coordination and memory loss. Hence a sensitive technique requires to detect the choline with in the suitable dynamic range along with good sensitivity. ECL can be used as one of the great analytical tools for sensitive and selective detection of choline in dynamic linear range over the other techniques. Valerie et al. demonstrated the ECL integrated FIA method as a fiber optic biosensor using luminol as a luminophore in detecting the choline at low level. The sensor assembly was constructed by connecting the flow system with fiber optics. Initially the choline oxidase was immobilized with diethylaminoethyl Sepharose-poly (vinyl alcohol) (DEAE-PVA) and then studied the ECL properties under various pH buffer and different flow rates. Similarly, different

![Figure 9. The enhancement in the ECL signal intensity of luminol/H$_2$O$_2$ system in the presence of microemulsion. Reproduced with the permission of ECS Sensors Plus, 2022 1 031604](image-url)
types of membranes like ABC membrane, UltraBind membrane, and PVA-SbQ gel were used to immobilize the choline oxidase enzyme for ECL analysis. Under the optimized FIA-ECL conditions the choline was detected with very low LOD and wide dynamic range. The following table shows the choline LOD and linear range with different immobilization support (Table I).

Further, the stability of the sensor was investigated for choline oxidase (ChOx) was immobilised either covalently on polyamide (ABC) membrane, UltraBind membrane, and DEAE-PVA-SbQ at applied potential of +425 mV vs Pt pseudo reference electrode, 3 nmol of choline with 0.5 ml min⁻¹ of flow rate. Among these, DEAE-Chx-PVA system shows good stability during 160 successive measurements over other systems with mean ECL signal of 267.5. Other FIA-ECL methods were developed for the rapid analysis of choline in urine sample by using luminol/H₂O₂ as a ECL probe. For example, Jiye et al. proposed new FIA for the choline detection by coupling ECL detector with the covalently immobilized ChOx on the aminopropyl-controlled pore glass (APCG) beads as an enzyme reactor. As seen in Fig. 10A.a, APCG beads were linked with glutaraldehyde by gentle stirring of mixer solution and then transferred into 0.1 M PBS containing 100 units of ChOx, the reaction was carried out 24 h at 4 °C. After the reaction, the ChOx/APCG was packed into a reactor which has 2 mm diameter and 10 mm length (Fig. 10A.b), and then the reactor was stored at 4 °C. The flow cell used for ECL-FIA analysis is shown in Fig. 10B, the luminol used as a carrier solution and the co-reactant H₂O₂ was generated by enzymatic reaction in enzyme reactor as shown below.

\[
\text{Choline} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{betaine} + 2\text{H}_2\text{O}_2
\]

The generated H₂O₂ was detected in the flow cell according to the following reaction.

\[
\text{Luminol} + \text{H}_2\text{O}_2 \rightarrow \text{light(425 nm)}
\]

The ECL intensity which is obtained by FIA-ECL method is directly proportional to the produced H₂O₂ concentration that means it also obviously proportional to the choline concentration. Under the optimized conditions, the proposed method shows linear increase of ECL intensity with the choline concentrations in the range of 0.1 μM to 1.5 μM with the LOD of 0.05 μM. The linear range and the LOD of choline detection obtained by this method is much lower than other methods. Hence, this proposed method used to detect the choline in urine sample, two sets of males and one set of female urine samples were used to detect the choline by spiking the known amount of choline into the diluted real sample. The results shown good recovery and comparable with microbore HPLC technique.

Detection of pharmaceutical drugs.—FIA-ECL has been used for the detection of pharmaceutical drugs like etamsylate, meloxicam, tetracyclines, and thiamazole with reasonable sensitivity, and wide dynamic range. Etamsylate is one of the eventually used pharmaceutical drug for prophylaxis which can be used to control the hemorrhaging in blood vessels. Rao et al. developed Ru(bpy)₃²⁺-Nafoi-modified carbon paste electrode (CPE) for FIA-ECL determination of etamsylate drug.95 The typical house-made FIA-ECL instrumentation for etamsylate detection is shown in Fig. 11A. The flow cell is made with Plexiglas with two flow channels of 2.0 mm diameter and 2.0 cm long. Two peristaltic pumps (p₁, p₂) were used to pump the phosphate buffer and etamsylate separately and then mixed stream was sent to the flow cell which is placed near to the PMT for ECL analysis (Fig. 11A and 11B). The preliminary cyclic voltammetry and ECL studies of Nafoi-CPE and Ru(bpy)₃²⁺-Nafoi-CPE is evidencing the enhancement of ECL intensity. This is due to the electrochemical reaction between Ru(bpy)₃²⁺ and etamsylate molecules. There is a redox peak of oxidation and reduction appears at 1130 and 986 mV for

| Immobilization support | Detection limit/pmol (S/N = 3) | Linear range | Cycle time/min |
|------------------------|-----------------------------|--------------|---------------|
| ABC membrane           | 300                         | 300 pmol to 30 nmol | 8             |
| UltraBind membrane     | 75                          | 75 pmol to 30 nmol  | 5             |
| PVA-SbQ gel            | 220                         | 220 pmol to 30 nmol | 3             |
| DEAE-PVA-SbQ           | 10                          | 10 pmol to 30 nmol  | 3             |

Figure 10. (A.a) ChOx immobilization on APCG beads and (A.b) schematic representation of enzyme reactor and (B) FIA-ECL design used for choline detection. Reprinted with the permission of94 Copyright © 2009 Elsevier B.V.
Ru(bpy)$_3^{2+}$-Nafion-CPE and no peaks were obtained for Nafion-CPE. The ECL intensity of Ru(bpy)$_3^{2+}$-Nafion-CPE is also 20-fold higher over the Nafion-CPE in the presence of etamsylate. The high ECL intensity of Ru(bpy)$_3^{2+}$-Nafion-CPE is observed at +1250 mV in the PBS of pH 9.0 with the flow rate of 2.0 ml min$^{-1}$. The optimized FIA-ECL method used to detect the etamsylate by recording the ECL intensity vs time transient curves. Figure 11C represents the ECL transient curves of Ru(bpy)$_3^{2+}$-Nafion-CPE in the presence of different etamsylate concentrations from 8.0 to 1000 ng ml$^{-1}$. ECL intensity gradually increases and attains maximum at 1000.0 ng ml$^{-1}$ with correlation co-efficient of 0.9997 (inset of Fig. 11C). The LOD of etamsylate is observed to be 1.57 ng ml$^{-1}$ with the signal to noise ratio of 3. The reproducibility of FIA-ECL towards etamsylate detection is also studied by fabricating seven different electrodes independently for 60, 200, and 1000 ng ml$^{-1}$ of etamsylate standard solutions (Fig. 11D). The results reveals that the proposed method has acceptable reproducibility with the relative standard deviation (RSD) values of 0.85 to 1.12%.

Thiamazole is a class of thio-compound and it can be used as a medicine in the treatment of Graves’ disease because it exhibits antithyroid activities which inhibits the production of thyroid hormones. But use of thiamazole causes serious side effects includes skin irritation, olfaction, allergies, and liver cirrhosis. Thiamazole has property of enhancing the water retention in animal’s cells and tissues, hence farmers’ uses thiamazole in feeding foods for animal. This may cause entry of thiamazole into human cells. It is a challenging task to detect such kind of harmful drugs in trace level. Kong et al. developed FIA-ECL technique to determine the thiamazole by using Ru(bpy)$_3^{2+}$ as a luminophore. The ECL of Ru(bpy)$_3^{2+}$ molecule get enhanced in the presence of thiamazole in alkaline electrolytic medium because of its co-reactant nature of thiamazole. This strategy was used to develop the simple and sensitive FIA-ECL method to detect the thiamazole in real samples of animal food. For the better sensor, FIA-ECL was studied under various optimized conditions of applied potential, different pH of PBS, at various flow rates and different Ru(bpy)$_3^{2+}$ concentrations. These studies confirm that, the sensitivity of FIA-ECL towards thiamazole sensor is better at applied potential of 1500 mV, PBS pH of 12 and 1.0 ml min$^{-1}$ flow rate with $1.0 \times 10^{-4}$ mol 1$^{-1}$ of Ru(bpy)$_3^{2+}$ concentration. The optimized conditions were used for FIA-ECL detection of thiamazole. Adopted FIA-ECL method shows the thiamazole detection with in the linear range of $2.0 \times 10^{-7}$ to $1.0 \times 10^{-4}$ mol 1$^{-1}$ with the LOD of $5.0 \times 10^{-7}$ mol 1$^{-1}$ (S/N = 3). Also, this method exhibits good reproducibility with the RSD of 0.75% for the consecutive ten tests in the presence of $5 \times 10^{-7}$ mol 1$^{-1}$ thiamazole. Further, thiamazole is detected in real samples like animal feed of chicken, duck and pig, the recovery of real sample is achieved in the range of 94 to 95.9%. The results obtained by FIA-ECL such as linear range, LOD is lower than well-known techniques like FI-CL, GC-MS and other electrochemical methods.

Most recently our group reported the FIA-ECL detection of dicyclohexylamine (DCHA) using luminol as the ECL probe. DCHA is also one of the pharmaceutical intermediate and it is an antibiotic residue in the harvested honey. The detection of DCHA is essential because it has genotoxic and tumorigenic properties. The well-known analytical techniques like revers-phase LC-MS and MS-based detection method were employed for DCHA detection, but these are highly sophisticated and requires huge time during analysis. The FIA-ECL is an alternate technique to detect the DCHA at trace amount. The developed FIA-ECL method is simple, sensitive, and highly selective for the DCHA detection. Figure 12A shows the schematic representation of DCHA detection in honey samples by FIA-ECL method. Luminol does not shows any ECL signal at +940 mV (ECL-2) in the absence of DCHA but high intense ECL signal is appeared in the presence of DCHA in dissolved O$_2$ of PBS (Fig. 12A). A week ECL
signal at +300 mV (ECL-1) is observed in the absence of DCHA and not influenced in the presence of DCHA. The reaction mechanism involving in the ECL of luminol in the presence of DCHA in dissolved O2 of PBS is given below.

\[
\text{LH}^- - e^- \rightarrow \text{L}^- + \text{H}^+ E_p = +380 \text{ mV vs Ag/AgCl} \quad [3]
\]

\[
\text{L}^- + \text{O}_2 = \text{O}_2^- + \text{L} \quad [4]
\]

\[
\text{L}^- + \text{O}_2^- \rightarrow \text{LO}_2^- \rightarrow \text{AP}^{2-} + \text{N}_2 + (\text{ECL - 1}) \quad [5]
\]

\[
\text{AP}^{2-} \rightarrow \text{AP}^{2-} + \text{hv (425 nm)} \quad [6]
\]

\[
\text{DCHA} \rightarrow \text{DCHA}^+ + e^- E_p = +940 \text{ mV vs Ag/AgCl} \quad [7]
\]

\[
\text{DCHA}^+ \rightarrow \text{DCHA}^+ + \text{H}^+ \quad [8]
\]

\[
\text{O}_2 + \text{DCHA}^+ \rightarrow \text{DCHA}^+ + \text{OOH}^- \quad [9]
\]

\[
\text{OOH}^- + \text{OH}^- - e^- \rightarrow \text{O}_2^- + \text{H}_2\text{O} \quad [10]
\]

\[
\text{L}^- + \text{O}_2 + \text{DCHA}^+ \rightarrow \text{AP}^{2-} + \text{N}_2 (\text{ECL - 2}) - \text{with O}_2 \quad [11]
\]

\[
\text{L}^- + \text{DCHA}^+ \rightarrow \text{AP}^{2-} + \text{N}_2 (\text{ECL - 2}) - \text{without O}_2 \quad [12]
\]

\[
\text{AP}^{2-} \rightarrow \text{AP}^{2-} + \text{hv (425 nm)} \quad [13]
\]

At first luminol get oxidizes to anion radical (L\(^-\)) which reacts with dissolved O\(_2\) to produce O\(_2\)^\(-\) and then excited 3-aminophthalate (AP\(^{2-}\)) formed due to the reaction between L\(^-\) and O\(_2\)^\(-\) which emits light (ECL-1). When DCHA is added into the solution, it gets oxidizes to DCHA^\(+\) and then converted into DCHA^\(+\) by reacting with dissolved O\(_2\) molecule. Finally, AP\(^{2-}\) will be formed by reaction of L\(^-\) and DCHA^\(+\) and then light emission occurs (ECL-
2). This ECL strategy is used to detect the DCHA by injecting into the carrier solution of luminol/PBS through the sample injector. The transient ECL signal (ECL-2) is recorded during each addition of DCHA with a flow rate of 0.25 mL min\(^{-1}\) in 0.1 M PBS along with the carrier solution of 0.1 \(\times 10^{-3}\) M luminol. Figure 12B shows the FIA-ECL transient curves (ECL-2) of 0.1 \(\times 10^{-3}\) M luminol at different DCHA additions in the range of \(1 \times 10^{-8}\) to \(1 \times 10^{-4}\) M. ECL intensity (ECL-2) gradually increases with each DCHA addition and the ECL intensity is linear with logarithmic concentrations of DCHA with regression coefficient of 0.9943 (Fig. 12C). This FIA-ECL method achieved the LOD of \(2 \times 10^{-9}\) M for DCHA (S/N = 3). Further DCHA was detected in real sample of honey by using standard addition method, the sample recovery is gained about average of 91%. Interference study was performed by taking glucose, fructose, ascorbic acid, folic acid, and riboflavin there was no effect of these molecules on ECL of luminol/DCHA system. This reveals that FIA-ECL method is highly sensitive and selective in DCHA detection.

**Determination of tetracyclines.** Tetracyclines (TCs) possess hydronaphthacene skeleton with huge number of functional groups.\(^{98}\) TCs are broad-spectrum antibiotics that can be used in medical purposes. The presence of TCs in foods can create allergic reactions, due to this determination of TCs in food analysis, and pharmaceuticals is an important and challenging task. Several methods have been reported to determine TCs, among those FIA-ECL is one of the fine and attractive method and possess highly sensitive with wide dynamic range. Pang et al. developed FIA-ECL method to detect TCs by adopting ECL inhibition strategy using Ru(bpy)\(^{3+}/TPrA\) system.\(^{66}\) FIA-ECL experiment performed by continuous pumping of solution containing TPrA, Ru(bpy)\(^{3+}\), and buffer at 3.0 ml min\(^{-1}\) through the carrier compartment. To gain the better sensitivity towards TCs detection, the ECL of Ru(bpy)\(^{3+}/TPrA\) system is optimized by controlling the flow rate, buffer pH, electrode potential, concentrations of Ru(bpy)\(^{3+}\) and TPrA. The optimized conditions of pH 8 (buffer), 1050 mV of electrode potential, and 5 \(\times 10^{-5}\) mol l\(^{-1}\) of Ru(bpy)\(^{3+}\) shows better ECL inhibition. TCs in real samples like Cortisone Eye Ointment, honey, and Chinese proprietary were detected by ECL inhibited method. ECL inhibition is occurring due to the energy transfer between electrochemically produced Ru(bpy)\(^{3+}\) and benzoquinone derivatives as shown in Fig. 13.

Even though, there have been plethora electrochemical-based methods developed for detection of immune assays,\(^{99}\) DNA analysis,\(^{100}\) drugs,\(^{101}\) pesticides,\(^{102-105}\) biomolecules,\(^{106-108}\) air contaminants,\(^{109,110}\) and heavy metal ions.\(^{101}\) Among those, the FIA-ECL based method is highly sensitive towards various sensor applications due to its low back ground noise, flow of analyte avoids

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*Figure 13. ECL mechanism involving in Ru(bpy)\(^{3+}/TPrA/TCs\) system. Reproduced with the permission of\(^{66}\) Copyright © 2005 John Wiley & Sons, Ltd.*
the byproducts accumulation on electrode surface, low cost, and easy to operate. Hence, developing the FIA-ECL strategy is essential for futuristic studies to environmental monitoring, and clinical diagnostics. The proposed review might be creates new ideas and helps to develop different FIA-ECL based sensor methods for point-of-care applications.

Conclusions

ECL grown as a powerful analytical tool and established as a dynamic technique in many analytical applications includes LEDs, biosensors, drug detection, and microfluidic based sensor devices, cancer cell analysis and fingerprint imaging etc. ECL also used in rapid COVID-19 analysis. Recently ECL shows an attractive glance in developing a variety of ECL-based sensors and more research articles are publishing every year. This development indicates that ECL is one of the attractive hot research areas. In contrast, the articles are publishing every year. This development indicates that ECL is one of the attractive hot research areas. In contrast, the articles are publishing every year. This development indicates that ECL is one of the attractive hot research areas. In contrast, the articles are publishing every year. This development indicates that ECL is one of the attractive hot research areas. In contrast, the articles are publishing every year. 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