



## Recent advances in catalyst-enhanced luminol chemiluminescence system and its environmental and chemical applications

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### ABSTRACT

Analyzing and measuring different macromolecules demands the use of chemiluminescence (CL) techniques. Several CL agents are available, with different degrees of biological sensitivity and use, such luminol, hydrogen peroxide, and oxalate derivatives. The article reviews the use of luminol chemiluminescence for environmental, chemical, and biological analytes. Even though chemiluminescent sensors have been investigated for more than 50 years, significant advances have been made in this area in the last 20 years, increasing their sensitivity. Based on the physicochemical characteristics of luminol, a comprehensive CL is dependent on a variety of parameters. Despite a considerable amount of study in this area, there remains a major demand for a sensitive and selective CL based sensing system for analytes. Sensitivity in these CL investigations necessitates a careful consideration of the optimal catalyst choices. Over the past 20 years, the catalysts for CL reactions have developed above conventional catalyst and now include bio-based catalyst and metal nanoparticles. This catalyst may offer enhanced sensitivity, selectivity, and stability through taking advantage of their large surface area. Furthermore, it can expand the scope of applications and provide unique perspective on the reaction mechanism. With regards to different chemical and environmental scientific investigations, and the sensing mechanisms of luminol CL with different catalytic systems, we have collected such a thorough overview of conventional catalysts, metal-based nano catalysts, and biobased catalysts in this review.

### 1. Introduction

Luminescence is a term of 'cold light' known since the beginning of human kind. Many natural luminescent phenomena like glowing trees, shining animals were thought to have religious significance. It is a phenomenon used to explain the process in which a molecule absorbs energy from an external source and emits that energy on relaxing from a higher energy to ground state [1]. In nineteenth century from the center of origin, a scientific analysis concerning luminescence was studied about luminescent organism such as bacteria in the sea, glow worms and fireflies [2]. The luminescence phenomenon first was ascribed to luminescent organisms by scientist G.C. Stokes in 1852. Stokes rule, which states that the wavelength of the light emission is higher than that of the exciting radiation, was established and it is currently known as the law of luminescence [3]. In 1888, Widemann introduced the term *Luminescence* (weak glow) comes from Latin (*lumen*=light). With the emission of

light, the molecule returns towards its ground state without absorption of energy.

Jablonski diagram depicts the various events that occur during the dissipation of absorbed light via radiative or non-radiative processes. There are various types of luminescence, each named after the source of excitation. Bioluminescence (BL), Photoluminescence (PL), Thermo luminescence (TL), Mechanoluminescence (ML), Electroluminescence (EL), and Chemiluminescence (CL) are examples of luminescence [4]. Furthermore, the responses of the probe molecules are influenced by a variety of environmental factors. Hennig Brandt published the first example of synthetic chemiluminescence [5]. After distilling urine, he extracted a chemical, with no prior light exposure he discovered the material to be glowing blue. He named this substance 'phosphorus mirabilis', or 'miraculous light'. Radziszewski, created the first synthetic chemiluminescent organic compound from pyrogallol in 1877. In the 20th century, many more CL molecules were observed, notably two

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among the most effective chemiluminescent compounds ever discovered. Albrecht discovered 5-amino-2,3-dihydrophthalazine-1,4-dione (luminol) in 1928, Gleu discovered di-methylid-acridinium nitrate (lucigenin) in 1935 [6]. Chemiluminescence (CL) commonly occurs if a chemical reaction yields a by-product that is stimulated and emits a photon after relaxing to the initial state. In the area of sensors, luminol had recently been discovered to be the most analytical technique. It is used as blood stain evidence in criminology while surface contaminated with blood traces, a mixture of luminol and oxidant can be sprayed [7]. Then it will glow when it reacts with a metal ion, such as iron in hemoglobin. Luminol chemiluminescence in forensics is shown in **Fig. 1**.

The cyclic peroxide decomposes during oxidation and reduction process between catalyst and hydrogen peroxide yield 3- amino phthalate in an excited state as well as a nitrogen molecule ( $N_2$ ). The ecstatic mood subsequently returns to the ground state of 3-aminophthalate, releasing blue glow at 435 nm. **Scheme 1** depicts the luminol chemiluminescence mechanism.

The discovery of luminol chemiluminescence is a useful tool with a broad range of applications in chemo sensors, biosensors, and immunoassays attributed to highly sensitive, broad linear region, convenient instrumentation, cost, and low backgrounds [8]. Even though that chemiluminescence evaluation has many advantages over the other optical techniques, like high sensitivity, a broad dynamic range, background noise, straightforward instrumentation, it has two major limitations: a general absence of knowledge of the chemiluminescent reaction mechanism and an absence of analyte selectivity. The first limitation makes it difficult to predict the chemiluminescence behaviors of a chemical species. Since several potential analytics can be detected by a chemiluminescent reaction, the selective detection of a single analyte is sometimes difficult to accomplish. Considering all this, it is believed that chemiluminogens, which detect light mainly through chemical oxidation, constitute a significant category of stimulus reactive soft matter, notably as self-reporting materials. Because of their high sensitivity and vast dynamic range, chemiluminogens have certainly offered up a variety of innovative technical uses which do not need sophisticated equipment (e.g., sensors, bio imaging materials, and light emitting diodes) among others [9]. Even though the field of Chemo sensors has been known for over 150 years, tremendous advances in the last two decades have been made with the emergence of optical sensors, which are now indispensable tools for sensing a wide range of biological, chemical, and environmental analytes. These probes detect in a straightforward, highly sensitive, selective, and specific manner. To detect analytes, these probes employ a variety of distinct mechanisms [10].

Perhaps because of sporadic attempts, there is no comprehensive overview covering the established catalytic system to initiate luminol CL and its detection limit. The selection of an appropriate catalyst is important for maximizing intensity in such CL studies. This review describes the incorporation of various catalysts for established luminol-hydrogen Peroxide ( $H_2O_2$ ) based CL systems to increase its sensitivity. Due to the lack of comprehensive overview, considering that luminol CL play a key role in sensing field due to its tunable properties, and the

catalytic system. We believe that a detailed overview for initiating the CL of luminol, and its sensitivity would be beneficial to a large community of scientists working in sensor fields. To simplify our overview of luminol CL's diverse catalytic systems, we have divided them into three categories: (i) Systems catalyzed by transition metals, such as potassium ferricyanide ( $K_3Fe(CN)_6$ ) [11],  $Cu^{2+}$  [12], and  $Co^{3+}$  [13]. (ii) Nano particles [14–17] (iii) bio-based catalyst [18]. The discussion of first category covers the transition metal catalyze the luminol CL systems, the major problem often encountered is the weak emission intensity results poor sensitivity. This section emphasizes the oxidation of luminol in alkaline medium takes place through various steps.

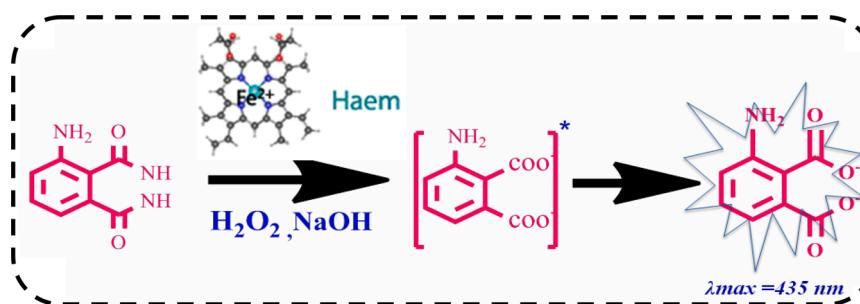
The luminol-CL system was successfully catalytic in the second category, in addition to metal-based catalysts, the use of nanoparticles due to their strong catalytic performance, conductivity, and huge specific surface area. The catalytic luminol-CL systems which were described do to operate in a similar way. In compared to the conventional transition metal-based method, though, no discernible improvement in CL intensity was found. Despite some recent attempts and significant recent progress in increasing CL and its sensitivity, there is currently no systematic review of this field in the literature. The last section of the review article discusses some bio-based (ecofriendly) catalysts made from a plant which has been shown to be highly sensitive to luminol oxidation. Furthermore, some of these catalysts work best when combined with an enhancer. However, extracting enzymes from plants is a costly process and a complex procedure. As a result, the sensitivity of the catalysts are unstable. The main objective of this review is the catalytic behaviour that has been used to enhance the luminol-CL system and its sensitivity. Three tables are presented, one for each of the three categories, listing the reported catalytic strategies for improving luminol-CL and its sensitivity. **Table 1**.

## 2. Transition metal catalyzed

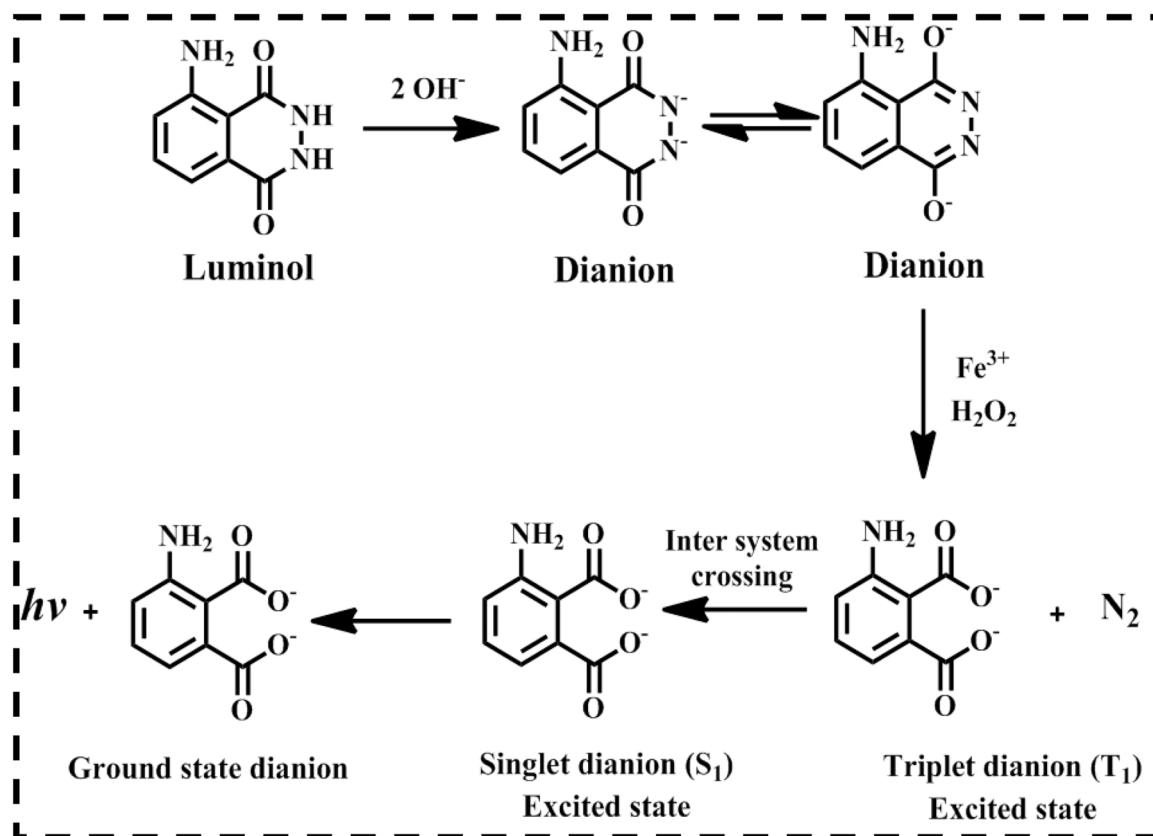
### 2.1. Conventional potassium ferricyanide ( $K_3Fe(CN)_6$ ) catalyzed chemiluminescence of luminol

Chemiluminescence (CL) has been shown to occur at 425 nm regarding luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) under a variety of circumstances. In general, luminol oxidation in alkaline medium occurs in a series of steps. After the initial formation of a dianion by the removal of two protons of phthalhydrazide groups, luminol forms strained endo peroxide intermediate with oxygen. This unstable endo peroxide gives an excited 3- amino phthalate with the removal of nitrogen. When the excited 3- amino phthalate gets relaxed to ground state it results in a weak blue light. In a few scientific and environmental applications, like immunoassays, metabolic pathway monitoring, free radical detection, trace metal analysis, as well as the detection of other inorganic chemicals, it is used as an analytical technique [19].

Luminol was discovered by Albrecht in 1928 to reveal blood stains in crime scenes. Seitz and Hercules first described the use of luminol CL as an analytical tool to detect Fe (II), the work of O'Sullivan and others has developed the technique for accurate and convenient measurement of Fe



**Fig. 1.** Luminol Chemiluminescence in forensics.



Scheme 1. Mechanism of luminol chemiluminescence.

(II) at naturally produced nano molar concentrations [20]. In general, basic solution of luminol shows chemiluminescence wavelength at 435 nm in the presence of iron (III) catalyst. The biggest problem often observed with this method is the weak emission intensity, pH of the system limits the applicability, and low sensitivity [21,22]. This system shows advantages like as amplification of luminol chemiluminescence and with no additional oxidants. Disapprovingly to increase the luminol CL, Iron based organic complexes like  $[\text{Fe}(\text{bpy})_3]^{2+}$  [23] complex ferric iron [Fe (III)] chelator, tetra nitrosoy iron complex with thiosulfate ligands was developed to oxidize the luminol CL intensity by hydrogen peroxide and thus often results same intensity and thus causing poor sensitivity towards analyte. The mechanism by which luminol oxidation results in CL is still poorly understood.

In order to increase intensity in such CL systems, it is essential to select the suitable catalyst to solve the aforementioned issues. For the past two decades, catalysts of CL reactions have been extended to other metal organic framework (MOF) (Fig. 2). A metal (Co)-Organic Framework (Co-MOF) was used to identify L-cystine is based on the luminol's chemiluminescence (CL) method, that enhances sensitivities [24]. It was detected selectively in the 0.1–10  $\mu\text{M}$  range, with an 18 nM detection threshold.

To raise the CL intensity of luminol, a solid catalyst, Fenqiang et al. [26] established functionalized MOFs by wrapping Hemin in HKUST-1 MOF materials [27,28] is shown in Fig. 3. Effective  $\text{H}_2\text{O}_2$  and glucose sensors with broad reaction ranges (7.5–750 M) and low limit of detection of 2  $\mu\text{M}$  were developed with Hemin@HKUST-1 composites.  $\text{Fe}_3\text{O}_4$ /MOFs were developed to shown to have excellent catalytic properties for directly catalyzing luminol chemiluminescence without the use of additional oxidants [29,30]. With a detection limit of 4.9 nM, this catalyst identified  $\text{H}_2\text{O}_2$  and glucose in a specimen of human serum.

The detection of hydrogen peroxide in rainwater recently used a green catalyst named Mg-Al-carbonate layered double hydroxides (LDH) via CL method [30]. A broad range of matrix interference ions in natural

water are more acceptable with the proposed method. If compared to luminol-peroxide based CL systems in flow injection systems, this method has a number of advantages, like high sensitivity, user friendliness, minimal environmental impact, and a low price. It is widely recognized that CL catalyzed with LDHs has enormous potential for environmental sample sensing.

Copper (II)-based organic compound, which can produce luminol- $\text{H}_2\text{O}_2$  to form a long-lasting CL emission, was loaded onto the paper surface [31]. Cu-PDA complex catalyst was produced by direct mixing and a fast-freeze-drying process. The Jahn-Teller distortion and uniform oval morphology of the Cu-PDA complex interact with a laminar microstructure to provide it a high level of catalytic properties and the capability to be embedded within in the cellulose pore. The slow diffusion technique enables long-lasting CL emission on the paper surface. The high CL intensity was produced by the complex high catalytic activity, which generated Reactive Oxygen Species (ROS) from  $\text{H}_2\text{O}_2$ . (Fig. 4A) Using the paper substrate makes it simple to adapt the flash-type luminol system to the long-duration CL system. With this long-lasting emission system, hydrogen sulfide was found using the CL imaging method. Future clinical CL imaging applications for this paper-based sensor are quite attractive. (Fig. 4B & C).

Reactive oxygen species (ROS) are important oxidizing species as a response of their having a variety of roles in ecosystems, including oxidative stress production, organism damage, and effective pollution removal. As a result, it is important to track the relative or real ROS concentration in the environment using an easy method. Since many investigations have documented the detection of ROS in various systems with CL methods and various catalyst, there has been a significant increase in interest from scientists in the use of CL for ROS detection. However, each of the reported methods corresponds to a specific reaction system, thus it is essential to evaluate the limitations of each method for the detection of different ROS species and evaluate the probability of their practical application. Using various catalyst with

**Table 1**Various catalyst used in luminol-  $\text{H}_2\text{O}_2$  CL and its applications.

Types of Catalyst	Proposed mechanism	Analyte	Detection limit	References
$[\text{Fe}(\text{bipy})_3]^{2+}$ complex	$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Iron (II)	$1.0 \times 10^{-9} \text{ M}$	[87]
Co-MOF	$\text{H}_2\text{O}_2 + \text{Co- MOF} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	L-cystine	18 nM	[88]
Hemin@HKUST-1	$\text{H}_2\text{O}_2 + \text{Co- MOF} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Glucose	2 $\mu\text{M}$	[89]
Mg-Al-carbonate	$\text{H}_2\text{O}_2 + \text{Mg- Al-Carbonate} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	$\text{H}_2\text{O}_2$ in Rainwater	0.02 $\mu\text{M}$	[90]
Cu-PDA complex	$\text{H}_2\text{O}_2 + \text{Cu-PDA} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	$\text{H}_2\text{S}$	0.05 $\mu\text{M}$	[91]
Fe-MOXs	$\text{H}_2\text{O}_2 + \text{Fe-MOXs} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	$\text{H}_2\text{O}_2$	20.4 nM	[92]
$\text{CoFe}_2\text{O}_4$	$\text{H}_2\text{O}_2 + \text{Fe-MOXs} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	$\text{H}_2\text{O}_2$	0.024 $\mu\text{M}$	[93]
$\text{Na}_2\text{MoO}_4$	$\text{H}_2\text{O}_2 + \text{Fe-MOXs} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Alucose in human serum	0.25 mol $\text{L}^{-1}$	[94]
Fe-N-SACs	$\text{Fe-N-SACs} + \text{Antigen} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	antigen	0.07 $\mu\text{M}$	[95]
MnO <sub>2</sub> nanosheets	$\text{MnO}_2 + \text{RNase H} \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	RNase H	0.0005 U $\text{mL}^{-1}$	[96]
Ag@ZIF-67	$\text{Ag@ZIF-67} + \text{antigen} \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Carcinoembryonic antigen	$4.53 \times 10^{-3} \text{ ng/mL}$	[97]
FeOOH Nanorods	$\text{FeOOH} + \text{uric acid} \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Uric Acid	6.3 nM	[56]
Cobalt oxyhydroxide nanoflakes	$\text{H}_2\text{O}_2 + \text{Cobalt oxyhydroxide nano} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Glutathione	6.4 nM	[98]
Black phosphorus quantum dots	$\text{H}_2\text{O}_2 + \text{Black phosphorus quantum dots} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Cobalt amount in rainwater	0.7 pmol/L	[99]
cobalt (II)	$\text{H}_2\text{O}_2 + \text{Cobalt (II)} \rightarrow \bullet\text{OH}, \bullet\text{OH} + \text{L} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Cysteine	9.8 3 1025 mol/ $\text{dm}^3$	[100]
GO	$\text{GO} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Glucose	0.044 mM	[101]
Graphitic carbon nitride	$\text{g-CN} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	2,4,6-trinitrotoluene	0.75 pM	[102]
Carbon dots	$\text{Carbon Dots} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	2-methoxyestradiol	$4.1 \times 10^{-10} \text{ g mL}^{-1}$	[64]
cupric oxide nanoparticles	$\text{Cupric Oxide nanoparticles} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Tannic acid in real Chinese gall samples	2.6 nM	[103]
Graphene-copper oxide nanocomposite	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Bisphenol-A (BPA) in feeding bottles	0.55 ng/mL	[104]
Gold nanoparticles	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Cholesterol	1.1 $\mu\text{M}$	[14]
Prussian Blue Nanoparticles	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Glucose	10 $\mu\text{g mL}^{-1}$	[105]
Disordered carbon catalyst	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	$\text{H}_2\text{O}_2$ in hair dye samples.	0.02 $\mu\text{M}$	[16]
Soybean peroxidase	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Peroxidase	0.3 pM	[84]
Sweet potato peroxidase	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	Peroxidase	1.01014 mol $\text{L}^{-1}$	[83]
Palm tree peroxidase	$\text{Graphene-copper oxide nanocomposite} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{O}_2^*, \bullet\text{OH}, \text{O}_2^{\bullet-} \rightarrow 3 \text{APA}^* \rightarrow 3 \text{APA} + h\nu$	HRP's	2 pM	[81]

Luminol, environmental applications of ROS generation and the use of ROS for pollutant removal have need to be developed further.

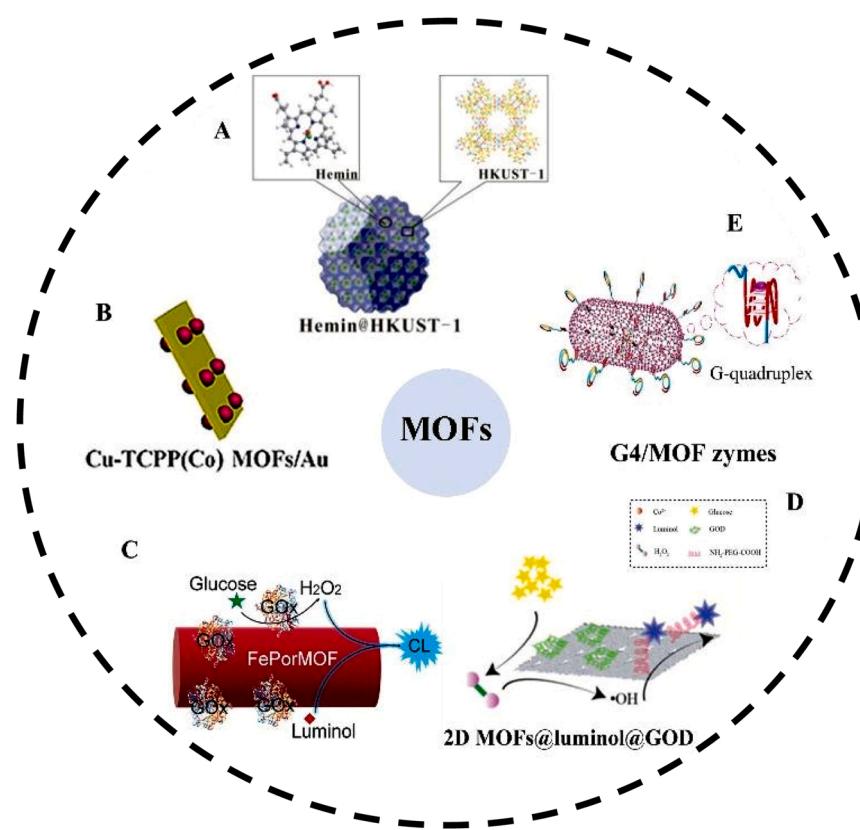
Iron ( $\text{Fe}^{3+}$ ) was used as the metal ion in metal-organic gels (MOGs), whereas 1, 10-phenanthroline-2,9-dicarboxylic acid (PDA) acted as the ligand. MOGs were discovered to have when the solvents were removed from luminol chemiluminescence (CL), good effect was obtained in the absence of other oxidants as hydrogen peroxide. Fe-MOXs-catalyzed luminol CL system, suggesting that the inherent oxidase-like enzymatic activity of Fe-MOXs on the oxidation of oxygen in the water is the source of luminol CL emission [20]. This method limit of detection is 20.4 nM was evaluated using dopamine quantitative study. With MOGs based on cyclodextrins and  $\text{CoFe}_2\text{O}_4$  and Iron (III) molecules, glucose and hydrogen peroxide was evaluated with a limit of detection was 0.024  $\mu\text{M}$  [33].

Recently, chemiluminescence of luminol enhanced in the presence of sodium molybdate ( $\text{Na}_2\text{MoO}_4$ ) CL mechanism investigation revealed that  $\text{Na}_2\text{MoO}_4$  increased the production of hydroxyl radical ( $\bullet\text{OH}$ ) and superoxide anion ( $\bullet\text{O}_2^{\bullet-}$ ) in the  $\text{H}_2\text{O}_2$ -luminol system, which could explain the enhanced-CL intensity and offered new insights into the CL-enhanced property of  $\text{Na}_2\text{MoO}_4$  [34]. The CL mechanism indicated that  $\text{Na}_2\text{MoO}_4$  enhanced the formation of superoxide anion ( $\bullet\text{O}_2^{\bullet-}$ ) and hydroxyl radical ( $\bullet\text{OH}$ ) in the  $\text{H}_2\text{O}_2$ -luminol system. This may explain the increased-CL intensity and gave us additional insight into  $\text{Na}_2\text{MoO}_4$  CL-enhanced property. The  $\text{Na}_2\text{MoO}_4$ - $\text{H}_2\text{O}_2$ -luminol system could be used to test glucose levels with the inclusion of glucose oxidase. With this catalyst, it has been possible to identify glucose in human serum

with satisfactory recoveries of 96.7%–105.4%. Despite their high catalytic activity, the synthesis of these metal organic framework catalysts requires multiple synthetic procedures, and some of these catalysts perform well only when an enhancer is present.

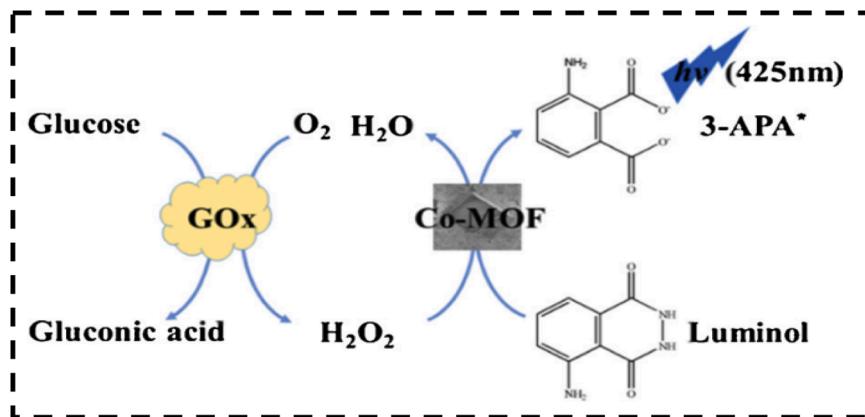
Li et al. [35] developed a first Fe (III) containing metal organic-xerogels (Fe-MOXs) to begin a luminol CL system without the requirement for additional oxidizing agents like hydrogen peroxide. The generation of free radicals increases significantly when an organic complexing agent is added to the experimental matrix, which has been shown to have an impact on CL intensity, often reducing but occasionally increasing the signals. This shows the relative intensity value when compared to other catalytic CL systems.

Recently, luminol single atom iron catalyst (Fe-N-SACs) and Fe, Co based dual single atom were used to increase the specificity and sensitivity of prostate-specific antigen detection with a linear range and a narrow detection limit [36] (Fig. 5). This catalytic system has a distinct electronic structure and exceptional properties for activating  $\text{H}_2\text{O}_2$  to generate massive reactive oxygen species (ROS). Cathodic electro-chemiluminescence always necessitates a more negative potential to produce strong emission, which inevitably damages target bioactivity and reduces sensitivity and specificity. The roles and relative importance of each of these processes are not well understood [37]. In earlier studies, either it was believed that organically complexed Fe (II) will induce luminol oxidation while it was not clear which form(s) of Fe (II) was intended to be measured. The full spectrum of organic and inorganic compounds containing Fe, however, is the analyte of the method, and



**Fig. 2.** Illustration of the MOFs based nanocomposites.

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**Fig. 3.** Schematic diagram of CL detection of glucose.

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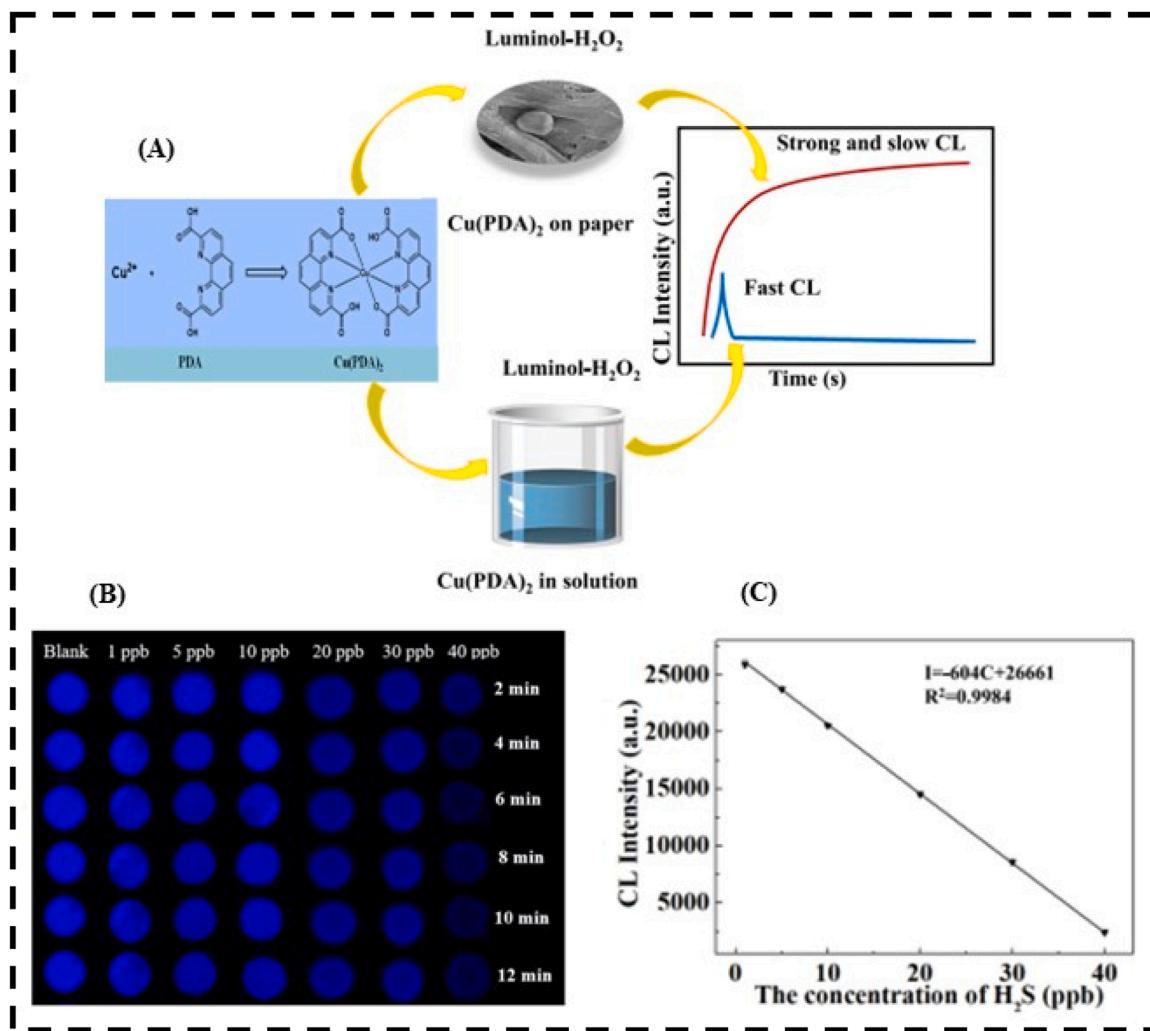
evidence suggested that organically complexed Fe (II) may contribute to the production of CL. This is supported by the fact that certain organics, like citrate, truly make the CL more intense. Thus, it is highly likely that the new system's modified oxidative would cause confusion by organic complexation. Even though the CL-based method still provides a strongly outlined calibration curve if organic material is present, it is uncertain if this curve is unique to the system being studied.

## 2.2. Metal catalyzed chemiluminescence of luminol

An extensive literature review finds that various ions, notably Co (II) [38], Cu (II) [39], Ni (II) [40], Cr (III) [41], Fe (II) [42], Rh (III) [43], and V (IV) [44], vastly improve the rate of this reaction (and hence the

chemiluminescence intensity), with Co (II) being the best rate modifier. It has been suggested that metal ions form complexes with luminol then oxidized by hydrogen peroxide. These metal ions are believed to have two distinct oxidation states. Among them, Co (II) was chosen for most efficient metal catalyst because, it has simple redox chemistry. When cobalt oxidation state can be either + 2 or + 3 and chromium oxidizes from + 3 to + 6, it can have intermediate + 4 and + 5 states. These oxidation states are thought to exist in aqueous solution.

Only addition of carbonate and hydrogen peroxide can significantly increase luminol chemiluminescence while Co (II) was catalyzing the reaction. The large CL enhancement is due to the influence of carbonate, which greatly increases the production of hydroxyl and carbonate radicals. This system used to analyze uric acid with the detection limit of  $10^{-5}$



**Fig. 4.** (A) Schematic diagram of CL with the luminol-H<sub>2</sub>O<sub>2</sub>-Cu-PDA Complex in solution and on paper. (B) CL imaging operated by an in vivo imaging system for H<sub>2</sub>S detection with a luminol-H<sub>2</sub>O<sub>2</sub>-Cu-PDA complex system. (C) Calibration curve with the concentrations of H<sub>2</sub>S vs CL signal intensities.

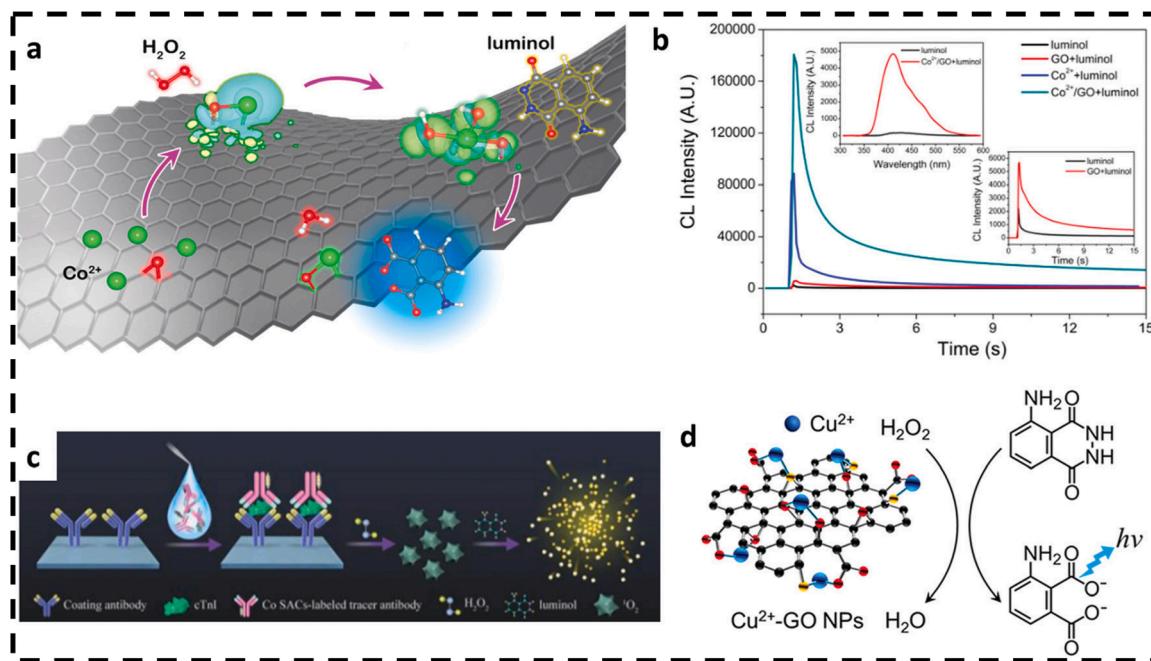
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<sup>12</sup> M [38]. The complexes of Mn (II) with amines and citrate/1, 10-phenanthroline stimulate strong chemiluminescence emission. This complexing agent is believed to stabilize the middle oxidation state of manganese, Mn (III). Superior catalytic activity was shown by synthesized Mn-based compounds toward the luminol-hydrogen peroxide CL system. Jiaqui et al. also developed a quantitative data analysis system with good sensitivity and selectivity for glucose and hydrogen peroxide sensing. Co (II)-ethanolamine complex [45], which would be partially submerged on Dowex-50 W resin, has been used as a heterogeneous catalyst for study its unbuffered or slightly acidic solution, luminol shows chemiluminescence (CL) in the presence of H<sub>2</sub>O<sub>2</sub>. The chemiluminescence intensity was enhanced to use this inorganic complex. A method by which CL emission in unbuffered solution occurs has indeed been postulated. If Co (II)-ethanolamine immobilized resin takes breakdown H<sub>2</sub>O<sub>2</sub>, a superoxide radical ion is produced as a byproduct. The major trends in between superoxide radical ion as well as luminol formed CL. Evaluating human urine and orange juice sample for glucose with good specificity and sensitivity. Furthermore to H<sub>2</sub>O<sub>2</sub> in precipitation with no additional preparation, the proposed method produces results which are acceptable.

High catalytic activity transition metal complexes immobilized in resin for the decomposition of H<sub>2</sub>O<sub>2</sub> have been reported. SbCl<sub>6</sub>-Cu (II)-amine, and Fe(CN)<sub>6</sub><sup>3-</sup> were used to enhance the chemiluminescence intensity of luminol Hexacyanoferrate (III) is particularly efficient, it was

used as a co-oxidant as well as a promoter in the CL production. These complexes are immobilized on Dowex-50 W resin [38], wherein retain strong across the decomposition process. The development of the peroxyo-metal complex has been hypothesized to contain an interaction in between transition metal complexes as well as a molecule of H<sub>2</sub>O<sub>2</sub> at the start of the reaction. To form an active intermediate, this complex then reacts with a new H<sub>2</sub>O<sub>2</sub> molecule. The complex then decomposes with O<sub>2</sub> evolution. The intermediates formed in the decomposition of H<sub>2</sub>O<sub>2</sub> catalyzed by a metal complex resin have still not been completely understood, substantial research into to the kinetics of H<sub>2</sub>O<sub>2</sub> decomposition with descriptions of applications ranging in chemical analysis [46].

The proposed metal ion complex oxidize luminol CL system has several drawbacks. First off, anthracene hydrazide and luminol have CL values that are nearly same. The reasons the CL decreases at high luminol concentrations is still unknown. Thankfully, a wide variety of catalysts were developed to oxidize luminol and produce enhanced chemiluminescence. As a result, poor selectivity can be observed in sensitivity luminol CL methods, and the exact moment at which luminol oxidizes into CL is unclear. Some luminol CL methods as a result had good sensitivity but low selectivity. However, the evidence is inconclusive, and the basis for this hypothesis is that luminol bidentate chelating agents, which coordinate with metal ions and one of the amino groups, and hydrazide carbonyl, form a 6-membered ring. The basic pH



**Fig. 5.** (a) Co single-ion catalyst for the CL reaction. (b) CL responses of different catalysts on luminol-H<sub>2</sub>O<sub>2</sub> reaction. (c) Schematic illustration of Co single-atom catalyst-based immunoassay of cTnI (d) Cu<sup>2+</sup>-GO NP enhanced CL reaction.

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required for luminol chemiluminescence limits the number of approaches available for studying the metal's role. Even if the analysis system is based on biological molecules like enzymes or binding proteins, the increased pH becomes an insoluble limitation, and peroxidase is discovered to be the preferred catalyst. The development of a neutral or weakly acidic luminol CL system is of high scientific value due to the importance of luminol in the field of CL research. Furthermore, despite the efforts of several analysts, establishing a homogeneous luminol-CL in neutral or acidic condition is difficult due to the chemical properties of H<sub>2</sub>O<sub>2</sub> and luminol. As a result, using the above catalytic system with luminol a fragile and costly device will be developed in future.

### 2.3. Nano materials catalyzed chemiluminescence of luminol

In the last two decades, catalysts for CL reactions have been extended to metal nanoparticles. Because of their large surface area, metal nanoparticles can provide increased sensitivity, selectivity, and stability [47]. Recently vast developments of nanomaterial and nanotechnology were developed. For the aim of boosting the Luminol-CL system, multiple nanoparticles were produced. Nanoparticles can act as reducing agents, catalysts, and luminophores in these systems to assist in CL reactions. They can also provide new insights into the reaction mechanism and broaden the scope [48–50]. In this context, from an in-depth literature survey reveals that, the nano particles catalyzed by luminol can be classified into Metal nanoparticles, Metal oxide nano particles, carbon based nano structures or dots and some nano composites have been reported to enhance CL of luminol.

### 3. Metal nanoparticles

The main drawback of traditional catalyst results poor selectivity. Researchers were found that metal nanoparticles catalyze chemiluminescence (CL) reactions due to their increased surface area, which gives them unique catalytic properties. The scientific community is interested in the use of nanoparticles to catalyze chemiluminescence reactions. Metal nanomaterials, particularly noble metals, such as silver,

gold, platinum, copper, tin [48,51–53] have properties related to their size and structure, which gives a promising future. Overall, Au metal nanoparticles have received a lot of attention as catalysts in CL reactions.

Chen et al. [54], reported the luminol-H<sub>2</sub>O<sub>2</sub> system's CL intensity could be enhanced in the presence of Ag nanoparticles, and then when compared to the absence of Ag NPs, the demonstrated that this catalyst can raise CL intensity. It has been discovered with Ag nanoparticles could catalyze the chemiluminescence of a luminol-hydrogen peroxide system. Catalytic activity of Ag was superior to Au and Pt colloid [48]. Superoxide anion or mono-dissociated hydrogen peroxide has been proposed as the backbone for the CL procedure, that reacts with luminol radicals and diazaquinone formed during the reaction with intermediate •OH decomposed by H<sub>2</sub>O<sub>2</sub>. This method used to catalyze cystine determination. Pt colloids were created on the luminol-H<sub>2</sub>O<sub>2</sub> CL system using the citrate and hydroborate reduction methods. Platinum nanoparticles produced using citrate reduction method whereas those produced to use the hydroborate reduction method did not show quite as much catalytic activity, was able to catalyze the CL from the luminol-H<sub>2</sub>O<sub>2</sub>. Several compounds reduced the luminol-H<sub>2</sub>O<sub>2</sub> citrate-protected Pt colloids system's CL signal. This method, which is using luminol-H<sub>2</sub>O<sub>2</sub> citrate to protect Pt colloids, discovered several components with good linear range and detection limits, showing the method excellent analytical potential. Zhi et al., were discovered that gold nanoparticles catalyzed luminol-H<sub>2</sub>O<sub>2</sub> system with an enhancement of CL signals. In interacting with a gold nano catalyst in this manner, the CL signal of luminol could be inhibited by some chemical compounds with hydroxyl, amino, or mercapto groups. However, this procedure similarly utilizes a comparable mechanism route. It is observed that these intermediate radicals with oxygen easily interact with the reducing groups in this situation, which are OH, NH<sub>2</sub>, or SH. A few intermediate radicals, most notably OH• and O<sub>2</sub>•, were generated during the reaction. These reducing extremely competitive for active oxygen intermediates, luminol, would probably lead to a decrease in CL intensity.

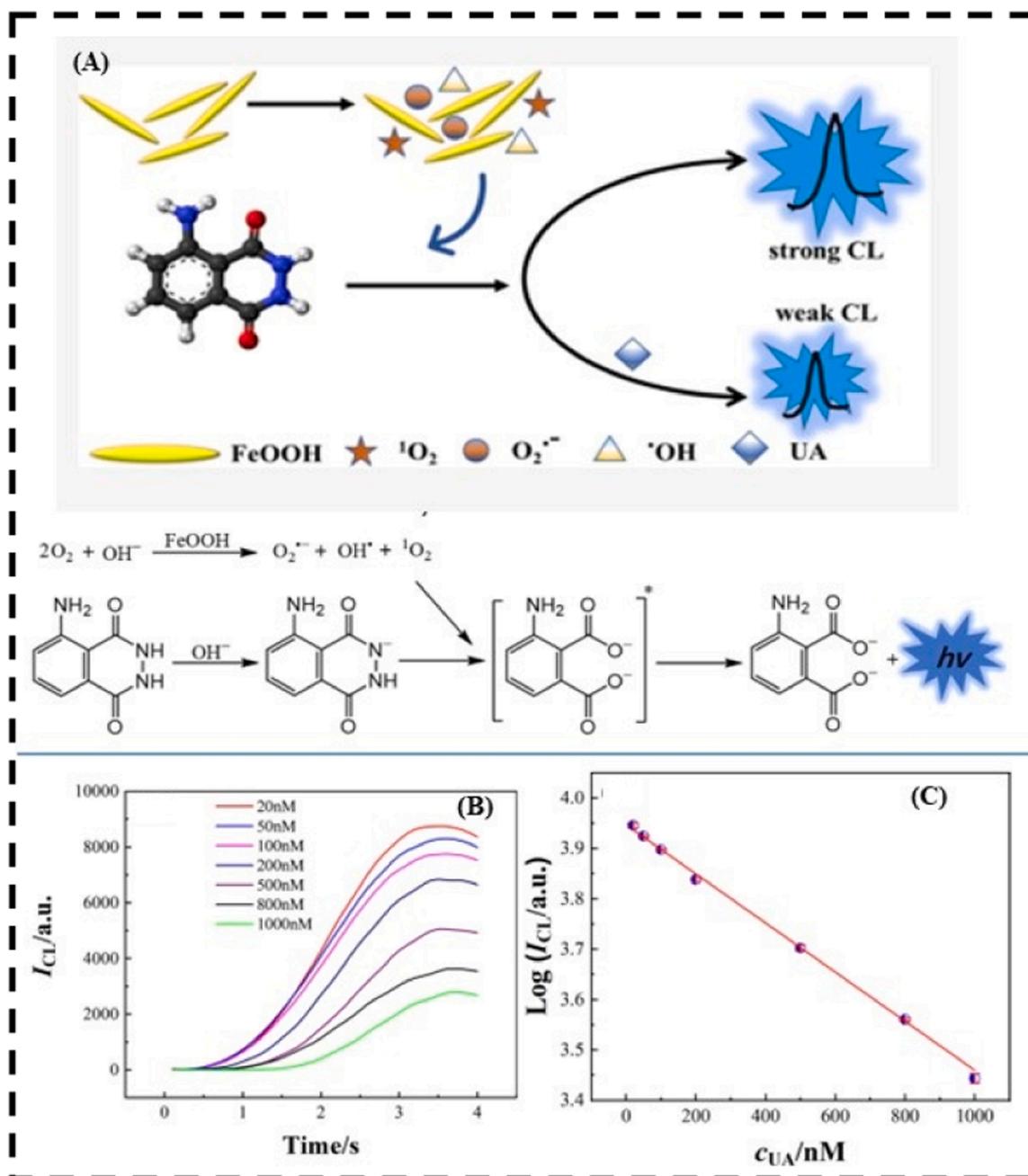
To circumvent the intricate synthetic method of catalyst, NiS nano was developed by a simple hydrothermal treatment and proposed to

catalyze Luminol system for the determination of vancomycin [55]. It was demonstrated that NiS nano catalyst could vastly improve the luminol- $O_2$  CL reaction. By utilizing this method vancomycin was determined and the proposed analytical method was validated with good sensitivity, linearity, and specificity. The advantages of all metal nano catalysts are high sensitivity, a wide dynamic range, flexibility of use, and cheap instrumentation costs.

The selective chemiluminescent sensors were developed to identify mercury (II) ions ( $Hg^{2+}$ ) in aquatic environment and soil supernatant samples using non-aggregated luminol-capped gold nanoparticles (AuNPs). Luminol-capped AuNPs can react with silver nitrate ( $AgNO_3$ ) in an alkaline environment and produce strong chemiluminescence (CL) emission because AuNPs showed excellent catalytic activity for the luminol- $AgNO_3$  CL system. Due to AuNPs' inherent affinity for  $Hg^{2+}$ ,

$Hg^{2+}$  would be adsorbed on the surface of luminol-capped AuNPs when  $Hg^{2+}$  was added to the solution of luminol-capped AuNPs. AuNPs' catalytic activity was significantly reduced in the presence of  $Hg^{2+}$ , that lead to CL quenching. The CL intensity gradually decreased as the  $Hg^{2+}$  concentration was increased. The produced CL sensor showed a strong linear relation in the range of 10–600 nM with a detection limit of 1 nM at a signal-to-noise ratio of three, which was below the maximum allowed concentration of  $Hg^{2+}$  in drinking water specified by United States Environmental Protection Agency (10 nM). As well, the developed CL sensor showed high selectivity for  $Hg^{2+}$  over other environmentally significant metal ions at high concentrations (500 M).

Because of its affordable price, abundance in nature, and renewability, a very significant number of nano catalysts have been developed to enhance the CL of luminol. The above catalysts are also widely used in



**Fig. 6.** (A) Schematic representation of enhanced luminol chemiluminescence with oxidase-like properties of  $FeOOH$  Nanorods; (B) CL emission-time curves at different concentrations of UA; (C) Linear relationship between log of CL peak intensity and the concentration of UA from 20 to 1000 nM. Reproduced by Ref. [57] from American Chemical Society 2023.

environmental monitoring, pollution prevention, and oxygen evolution reaction electrocatalysis because of their unique electronic and magnetic properties. Whereas all these nanoparticles use a similar catalytic path in a multi-step CL emission process, the result is poor sensitivity and selectivity. We determine that although the methods for producing noble metal nanoparticles, such as silver, gold, and platinum, were easy, the cost was relatively high.

### 3.1. Metal oxide nano catalyst

So, researchers, decided to develop a with a cheap metal oxide nanoparticle such as  $ZnO$ ,  $Fe_2O_3$ ,  $CoFe_2O_4$ ,  $CuO$ ,  $Co_3O_4$ ,  $MnO_2$ , and Metal nanoclusters (NCs) like Ag NCs, Au NCs, and Cu NCs which decided to provide new understanding of the catalytic reaction and extend the applications of it [34]. These metal oxide catalysts and metal because of their high concentration of unsaturated metal sites, nanoclusters have been shown to have strong catalytic activity in the luminol- $H_2O_2$  CL process. Dejian et al., have proposed that Co-MOF catalyst was prepared using hydrothermal method and used to catalyze luminal-CL system. It exhibits peroxidase-like characteristics as a catalyst. The suggested catalyst's mechanism shows a basic pathway, and it increases the decomposition of  $O_2$ , it improves the luminol- $H_2O_2$  reaction's CL emission, which is designed to evaluate the detection of glucose in human serum and urine samples. Recently Li et al. [56], functionalized  $ZnO$  nano with a high catalytic performance was developed for luminol electrochemiluminescence immunosensor. This catalyst effectively catalyzed the development of  $H_2O_2$  in-situ as a luminol co-reactant, increasing luminol ECL signals and promoting luminol ECL responses. Ji et al. [57] have synthesized FeOOH nanorods in a simple and environmentally friendly one-pot hydrothermal method and used as a catalyst for the first time to generate strong CL with luminol without the use of an additional oxidant. Surprisingly, the luminol-FeOOH system has approximately 250 times the CL of the luminol- $H_2O_2$  system. He proposed that the developed method is a simple, fast, sensitive, and selective CL method for uric acid detection with a linear range of 201000 nM and a detection limit of 6.3 nM (S/N = 3). In Fig. 6(A) reveals that luminol with dissolved oxygen produces little CL, whereas the addition of FeOOH nanorods produces strong CL that is approximately 250 times that of the luminol- $H_2O_2$  system, indicating that FeOOH nanorods have excellent catalytic properties for luminol CL. Several common radical scavengers were used to reveal the roles of superoxide anion radicals ( $O_2^\bullet$ ), hydroxyl radicals ( $OH^\bullet$ ), and singlet oxygen ( $^1O_2$ ) on CL intensity to further reveal the CL mechanism of the luminol-catalytic system. Superoxide dismutase (SOD) and sodium benzoate are specific radical scavengers for superoxide anion radical ( $O_2^\bullet$ ). In the case of FeOOH nanorods can catalyzed dissolved oxygen to generate a large amount of reactive oxygen species (ROS), which then interact with luminol anion to produce the excited-state, 3-aminophthalate (3-APA $^*$ ) ultimately, this intermediate returns to the ground state, yielding a powerful CL [Fig. 6 (A)].

The assessment of environmental risks and the protection of human health depend critically on the practical detection of single-component pesticide residue at ultra-low concentrations in agricultural products and the environment. Using a synergistic co-catalysis of graphene oxide (GO)/gold nanoparticles (AuNPs) nanocomposites for the luminol CL reaction and the smart interface engineering, an efficient and highly sensitive chemiluminescence (CL) sensing acetamiprid in agricultural products and environmental media was developed. Dimensional changes in the aptamer conformation were re-established upon addition of acetamiprid, allowing the synergistic catalytic amplification signal of GO/AuNPs to function normally once again. 8.9 pM was the minimum amount detectable.

The excellent sensitivities may be attributed by the synergistic catalysis of GO/AuNPs for the CL reaction and the perfect modulation of the composite interface by DNA dimension. The GO/AuNPs maintained its stability for six months, which was longer than any other AuNPs that

had been reported until that point (only half a month). In the analysis, acetamiprid demonstrated exceptional selectivity. Results of sample size detection test shows functionality. This technique is extremely helpful for analyzing the quantities of pesticides in the environment and food goods, a very essential function. Novel interface engineering and the cooperative co-catalysis of GO/AuNPs offer promising directions for the development of biosensors. (Fig. 7).

As per recent studies,  $MnO_2$  and  $MoS_2$  nanomaterials are ideal candidates for catalyzing the decomposition of  $H_2O_2$ , which is attributed to an increase in electron-electron correlations that assists in planar electric transportation characteristics [59].  $TiO_2$  has attracted its most attention among all metal oxide nano catalysts owing to its sizeable surface area, high surface adsorption, stability, and biocompatibility [60]. To the greatest of our knowledge, these metal oxides outperformed a single nanoparticle catalyst because of their extensive surface adsorption.

### 3.2. Carbon based nano catalysts

Depending on their catalysis on luminol compounds, in a wide range of domains, CL strategies have been developed or used extensively, include bioanalysis and food analysis. The luminol- $H_2O_2$  CL reaction is essential, so elucidating the chemiluminescent mechanism has attracted a lot of attention. In a review by Branett and Francis, the CL-production procedure from the luminol- $H_2O_2$  includes a complicated multistep method. The superoxide anion radical ( $O_2^\bullet$ ) and hydroxyl radical ( $OH^\bullet$ ) have been numerous mechanisms in luminol oxidation processes. Afterwards when, this  $OH^\bullet$  reacts with the luminol to form an intermediate, that leads to enhanced CL. In fact, a comprehensive examination of the relevant literature revealed that singlet oxygen ( $O_2$ ) did not lead to the higher CL of luminol-only  $O_2$  and  $OH^\bullet$  contributed showed in Fig. 4. Despite the fact, that luminol CL has been reported a very low CL efficiency. Hao et al. were the first to identify graphene oxide (GO) as an efficient luminol-CL catalyst due to its well-defined honeycomb structure. Outstanding catalytic activity, conductivity, and a huge specific surface area all seem to be characteristics of GO (Fig. 8). So, until now, the primary uses of carbon nanomaterials in catalysts acted as metal-free catalysts or supporting for immobilizing catalytically active compounds. An electron transfer accelerator is generated by intrinsic catalysis of GO, which lead to the predominance of  $O_2$  and the enhanced CL of luminol [61].

Liu et al. [62]. report the carbon nanodots (CDs), a new class of discontinuous or almost spherical carbon nanomaterial with dimensions less than 10 nm, exceed heavy-metal-based quantum dots in terms of good photoactivity, nontoxicity, bio - compatibility, and low price. Cetyl trimethyl ammonium bromide-passivated carbon nanodots (CTAB-CDs) were made by adding CTAB to a clean hydrothermal treatment of fullerene ( $C_{60}$ ). It was proposed that mechanisms behind luminol-CL system catalyzed with GO and CDs is similar to that of metal nanoparticle catalysis. However, as compared with catalysis that used a conventional method, there wasn't apparent improvement in CL intensity [63–66]. CL systems with carbon nanodots [67], graphene [68], carbon nanosheets [69], and quantum dots [70] have also been reported as a result of their work. However, the quantum yield of these carbon-based catalyst-luminol- $H_2O_2$  systems was low. (An eight-fold increase in CL intensity). Disordered carbon is a type of carbon that is the most common in nature. It has been used in sensors, adsorbent materials, super capacitors, and corrosion inhibitors [71]. Synthesis of Carbon nano dots, graphene, carbon nano sheets, and quantum dots were complex processes that resulted in the release of toxic gases [72].

Simon et al. [16] have synthesized a disordered carbon catalyst by hydrothermal treatment of *Moringa Oleifera* to activate the luminol-CL system without an enhancement. The limit of detection of hydrogen peroxide was estimated to be 0.02  $\mu M$  in ideal circumstances, demonstrating that catalyst was extremely sensitive to the gases. According with author, a variety of analytical applications can use recommended

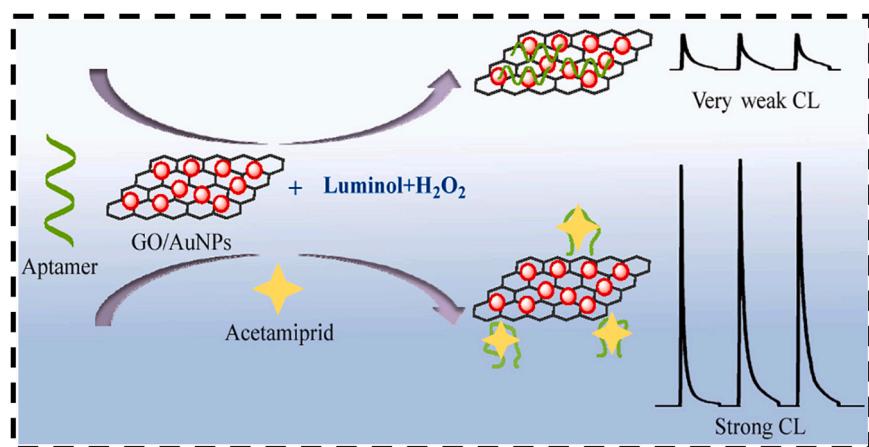


Fig. 7. CL Mechanism of Luminol Catalyzed by GO/AuNPs.

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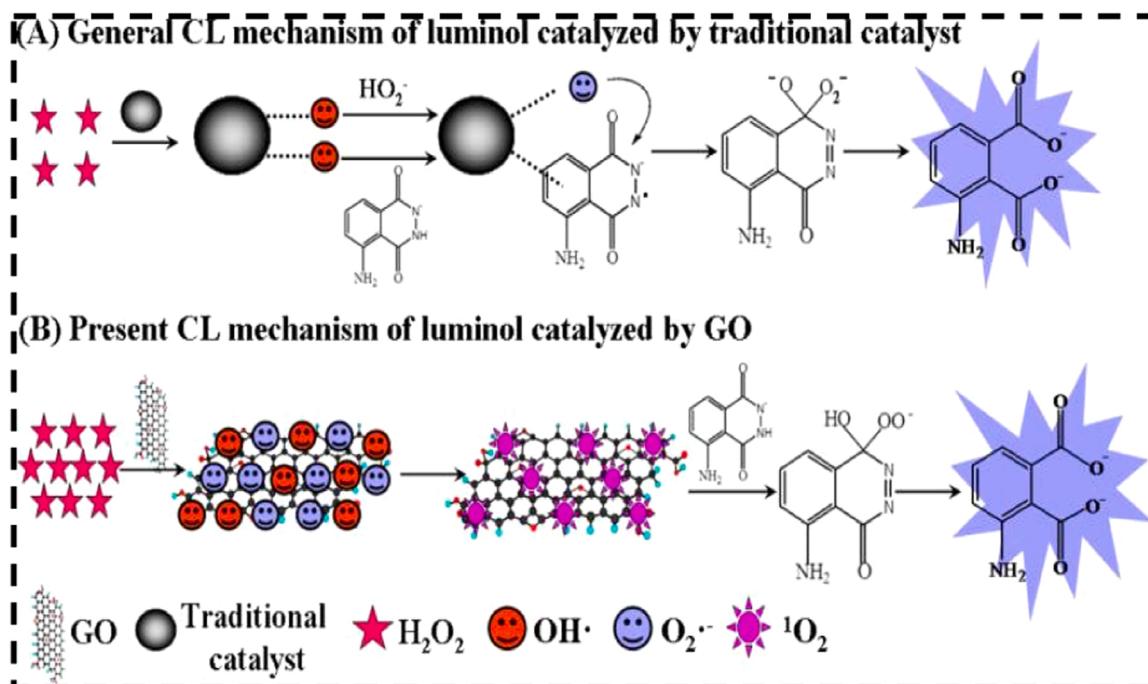


Fig. 8. Comparison of the CL mechanism of luminol catalyzed by traditional catalyst (A) and GO (B).

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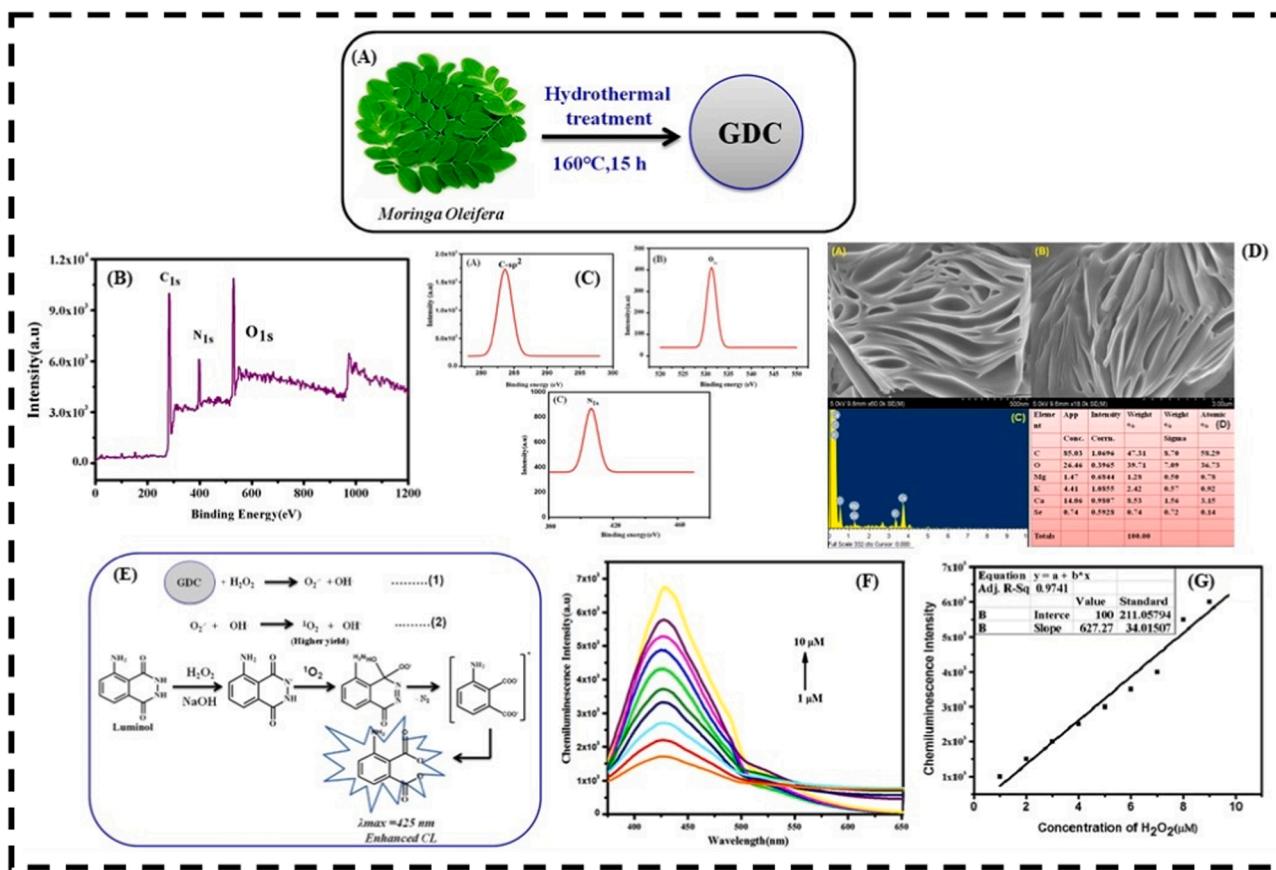
low-cost, ecologically acceptable, and nontoxic catalyst to detect hydrogen peroxide. This nanomaterial acts in the CL synthesis of the luminol- $H_2O_2$  system as a catalyst. Decomposition of  $H_2O_2$  to produce  $OH\cdot$  and  $O_2\cdot$ . Therefore, a considerable amount of singlet oxygen will be formed by combination of these intermediate linked to oxygen ( $O_2$ ). The rapid reaction of  $O_2$  with luminol during luminol oxidation causes the formation of an unstable endoperoxide.

Once this endoperoxide recovers to its ground state, the high-energy 3-aminophthalate moiety emits light. So, it was also investigated on how oxygen impacted the CL response. After nitrogen and oxygen was bubbling into the reaction solution, the CL intensity changed significantly compared to air environment, decreasing by 60% in the nitrogen environment and increasing by 40% in the oxidative environment. The result shows that oxygen is essential to the CL procedure. It should be clearly stated that while nitrogen bubbling can reduce the amount of oxygen in the reaction solution, a completely oxygen-free solution is not feasible [73]. As a result, the nitrogen blowing lowered the CL but did

not entirely get clear of that too. Nano dots, some nano composites, and layered nano structures (GO, Co-Ni layered double hydroxides), all have been seen to strengthen luminol's CL intensity.

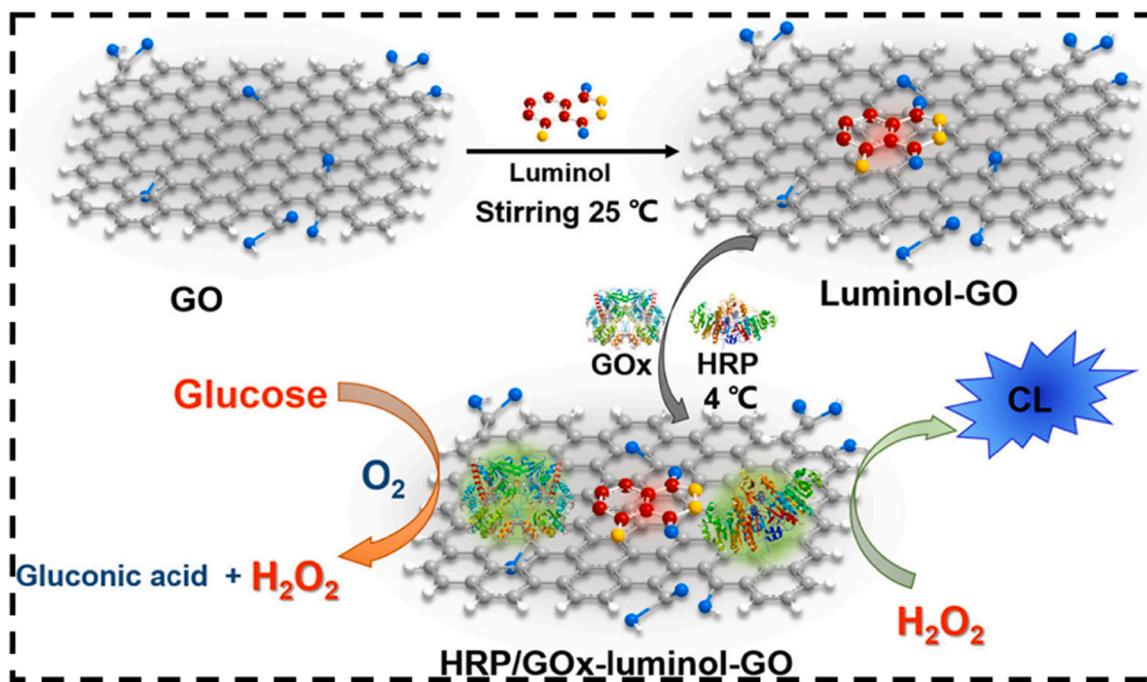
### 3.3. Bio based catalyst

Peroxidase is among the best-known plant enzymes. Peroxidase isozyme C is a common enzyme-linked immunosorbent test (ELISA) for clinical, food, and environmental measurements (HRP-C). HRP-C is enzyme labels used for immunochemical reagents [73]. Various methods were used to detect the enzyme activity of peroxidase-labeled immune reagents. Among them CL method is significantly more sensitive than other methods because it has been widely used to determine vitamins, proteins and nucleic acids. Weak signals, low intensity, and limited luminescence duration are just a few of drawbacks with in previous luminol CL assay (Fig. 9). Scientists discovered new environmentally friendly and long-lasting catalysts, like anionic peroxidase



**Fig. 9.** (A) Synthesis of green disordered carbon (GDC) (B). XPS spectrum of GDC (C). Deconvoluted XPS spectra of C1s, O1s, and N1s (D). SEM-image of GDC, EDAX data of GDC (E). Possible mechanism of the enhanced CL reaction. (F) Linear response range for  $\text{H}_2\text{O}_2$  detection in hair dye samples.

Reproduced by Ref. [16] from Wiley 2022.



**Fig. 10.** Schematic illustration for the assembly of HRP/GOx/luminol-GO and fabrication of CL biosensor.

Reproduced by Ref. [74] from Springer 2018.

derived from plants, in order to overcome these challenges, to be especially sensitive in the absence of any enhancer in the oxidation of luminol. For increased CL intensity in HRP-catalyzed luminol CL systems, an enhancer must be added to the substrate combination owing to HRP's poor catalytic capacity. Researchers have shown that certain plants or fungi, including HRP peroxidase, can efficiently catalyze luminol oxidation even in the absence of enhancer. These approaches for peroxidase-based CL testing demonstrate their value for identifying analytes in a variety of disciplines, including as illness diagnostics, food analysis, and environmental monitoring [75,76]. The speed of this reaction and, consequently, the intensity of the chemiluminescence are significantly increased with various peroxidases, a thorough literature review revealed. Horseradish peroxidase (HRP) is widely used in a variety of applications, like the identification of  $H_2O_2$ , through linked enzymatic reactions, nucleic acids as well as other macromolecules, the elimination of toxic chemical compounds from water. In these practical uses, HRP (mainly HRP-C, the isozyme c of horseradish peroxidase) serves as a starting point for the luminol CL reaction. Since HRP is a poor catalyst for luminol oxidation by  $H_2O_2$ , the CL intensity must be raised with enhancers. It's also been noted that the enhanced CL reaction offers notably higher sensitivity, light intensity, as well as more stable and continuous light emission.

In addition, the luminophore in the HRP-catalyzed [77] luminol- $H_2O_2$  CL system has been identified as the excited-state 3-amino-phthalate anion (3-APA $^*$ ). Although the presence of enhancers enhances CL intensity due to their higher concentrations, it does not generate a new luminophore since they have a lower reactivity towards peroxidase and oxidized intermediates of peroxidase than luminol.

These anionic peroxidases have been reported to be effective catalysts for luminol oxidation by  $H_2O_2$  in the absence of enhancers, in comparison to some of the most often used catalysts HRP. The intricate chemical reaction's inactivation of HRP was the main factor in the rapid light degradation. Several researchers had attempted to get a fairly constant light signal. Several range of anionic peroxidases, like palm tree peroxidase (PTP), sweet potato peroxidase (SPP), soybean peroxidase (SbP), and *Jatropha curcas* peroxidase, have indeed been introduced into luminol-based CL system (JcGP1). The detection of substances to use a new enhanced anionic peroxidase-catalyzed luminol CL method is currently being performed, including mouse immunoglobulin G, human chorionic gonadotrophin, and ochratoxin A [78].

### 3.3.1. Soybean peroxidase-catalyzed luminol- $H_2O_2$ chemiluminescence system

Sessa and Anderson were the first to isolate and purify soybean peroxidase (SbP) from soybeans. The excellent catalytic performance of SbP in the luminol- $H_2O_2$  CL reaction was recently proved. This novel SbP-luminol- $H_2O_2$  CL system has been used to develop a straightforward but effective peroxidase detection method. After HRP was switched out and for SbP, with a detection limit as low as 0.3 pM, the novel techniques to evaluate remarkably sensitive CL detection of SbP [79]. Due to SbP's excellent catalytic activity in the absence of enhancers, the sensitive CL-ELISA for determining mice IgG is developed by Sakharov et al. Comparing to HRP conjugate, SbP and anti-mouse IgG antibody conjugation offered a noticeably slower growth rate of light degradation. Zhao et al. used the CL method to detect chorionic gonadotrophin, [80] demonstrating that it had broad linear range of 0.18–18 ng mL $^{-1}$  and a low detection limit of 0.07 ng mL $^{-1}$ . A good alternative for identifying ochratoxin A also was suggested to be the SbP-catalyzed luminol- $H_2O_2$ -MORP-SPTZ CL system (OTA) [81]. Additionally, the recently established competing CL-ELISA method demonstrated sensitivity when compared to the conventional colorimetric ELISA methods. When using such a system to the detection limit and working range of OTA in food samples were observed to be 0.01 ng mL $^{-1}$  and 0.02–0.3 ng mL $^{-1}$ , accordingly. The 2,4-dichlorophenoxyacetic acid (2,4-D) may be determined accurately to use a direct competitive CL-ELISA, as according to study by Vdovenko et al. [82]. Based on the aforementioned

quantitative analysis method, the 2,4-D limit of detection was 1.5 ng mL $^{-1}$ , with a broad operating range of 6.5–545 ng mL $^{-1}$  [83]. The method is quite likely to be effective in identifying immunoassays.

### 3.3.2. Sweet potato peroxidase-catalyzed luminol- $H_2O_2$ chemiluminescence system

In addition to SbP, sweet potato peroxidase (SPP) also was proven to positively enhance luminol oxidation by  $H_2O_2$ . In fact, the stable, long-lasting CL signal was produced due in large part to SPP's noticeable decreased rate of light degradation. Moreover, pH 7.8–7.9 was the pH where the SPP-catalyzed luminol CL system generated its most light. Furthermore, as compared to other peroxidases (PTP, SbP, and HRP-C), the pH range was lower. The high sensitivity method called, in ideal circumstances, identifies SPP at a limit as low as 1.01014 mol L $^{-1}$ . The results indicate that an SPP is determined using a novel CL system, as reported by Vdovenko et al. In raise the brightness, co-enhancers like intensity, SPTZ, and MORP were added. SPP detection is sensitive with such a detection limit of 0.09 pM. The detection limit was ten times lower with this technique as compared with the traditional PIP enhanced HRP-catalyzed luminol CL system [76]. Because it combines the enhancement feature of SPTZ and MORP co-enhancers with the excellent photocatalytic performance of SPP, the novel system demonstrates tremendous potential for the ultra-sensitive detection of some chemicals in immunoassays.

### 3.3.3. Palm tree peroxidase-catalyzed luminol- $H_2O_2$ chemiluminescence system

The addition of palm tree peroxidase (PTP) to the luminol oxidation by  $H_2O_2$  method was first reported by Sakharov et al. due to rapid development of an anionic plant peroxidase-catalyzed CL system. *Elaeis guineensis*, an African oil palm tree, grows leaves and used to isolate the palm peroxidase (AOPTP). Surprisingly, this was discovered by the researchers that adding HRP enhancers like PIP and pCA had no effect on the AOPTP-catalyzed luminol CL system. The AOPTP-catalyzed luminol CL system may exhibit a detection limit value for AOPTP of 2 pM in the absence of any enhancer owing to AOPTP's higher catalytic activity than HRP. Development of sensitive enzyme immunoassay kits has been facilitated by the outstanding stability of AOPTP and the extended CL signal provided by the AOPTP- $H_2O_2$ -luminol CL system. Sakharov et al. shown that royal palm leaf peroxidase can effectively produce a long-term CL signal with a detection limit as low as 1 pM, in contrast to AOPTP [84]. Also, the pH range of 8.3–8.6 which was near to HRP's optimum pH range, showed the high radiation light. Additionally, it was revealed that this royal palm leaf peroxidase became very stable, indicating that analytical studies certainly held a promising future for that.

### 3.3.4. Other peroxidases as catalysts in luminol- $H_2O_2$ chemiluminescence system

*Jatropha curcas* peroxidase (JcGP1) and tobacco peroxidase are two more anionic plant peroxidases with catalytic activity in the luminol CL system (TOP) [85]. TOP isolated from transgenic tobacco plants has previously found to contain a strong catalyst for luminol- $H_2O_2$  CL reaction. The study of the signal-to-noise ratio's pH dependence revealed a pH range of 9.3–9.5 as the optimal range for TOP-induced luminol oxidation by  $H_2O_2$ . TOP's rate constants for the oxidation of luminol by intermediates were very close to those of other peroxidases (like HRP and *Arthromyces ramosus* peroxidase (ARP), their rate constants for the reduction of intermediates were very different. The suggested method offered a highly sensitive CL detection of TOP with a limit of detection of 0.1 pM at the specified pH and other ideal conditions. JcGP1 was later discovered and used in the luminol- $H_2O_2$  CL system because of its high electrocatalytic activity. The JcGP1-catalyzed CL reaction didn't require enhancer, in opposed to HRP. Furthermore, the JcGP1-induced CL system wasn't really greatly affected by PIP. The proposed method might provide a sustained CL signal. The detection limit was established at 0.2 pM via tests in different conditions. To use the results from of the new

ELISA kits, a basic JcGP1-luminol-H<sub>2</sub>O<sub>2</sub> system would be developed. A catalyst composed of bio-based cationic liposomes was used by Fan and coworkers. It was reported that luminol efficiency of these catalysts, in particular, can be enhanced without the need for enhancers as they were very sensitive, stable, and selective. Spite of strong catalytic activity, the difficulty of the synthetic processes is a major source of concern. Some of these catalysts typically perform best in conjunction with an enhancer. On the other hand, extracting enzyme from plants is indeed an expensive procedure. Enzyme-based catalysts also are unstable due to how sensitive these are to temperature and pH. Vanillin has been shown to dissociate H<sub>2</sub>O<sub>2</sub> into active •OH and O<sub>2</sub>• radicals in an alkaline aqueous solution [86], which speeds up the luminol-H<sub>2</sub>O<sub>2</sub> reaction and provides a strong CL signal in addition to the catalysts.

The authors suggested an approach to taken advantage of vanillin's catalytic function to increase luminol-H<sub>2</sub>O<sub>2</sub> chemiluminescence by two signals at once. As vanillin is hazardous to humans at high doses, it is essential to determine this unique flavor compound before applying it as a food additive. It has been intended to identify vanillin to use a low-cost, fast, and simple CL sensor based on the luminol-H<sub>2</sub>O<sub>2</sub>/Vanillin reaction. For vanillin over a concentration range of 1.0–75 M, the sensor had a detection limit of 0.89 M (S/N = 3).

#### 4. Conclusion

The review discussed a few improved catalyzed luminol CL systems that could offer remarkably low detection thresholds and high light intensities for a variety of analytes. Through the progress in the development of Chemiluminescence (CL) based sensors using various catalyzed luminol CL systems that have been reported for analysis and determination in a variety of fields. The use of different catalyst-based CL in environmental analysis has been the subject of extensive research. This review had reached an agreement about CL principle, the functions of the catalyst in the CL system, and the application to chemical and environmental research. There are a few problems despite this beneficial advancement.

To develop a more advanced device with increased detection sensitivity, though, needs to overcome lots of challenges. The following criteria could be fulfilled with the aid of CL-based sensors. (i) High sensitivity: Enhancing sensitivity is a constant goal in the development of sensor, especially for medical and diagnostic uses where spotting disease progression early on is crucial to significantly lowering morbidity and mortality rates. (ii) High selectivity: While most CL based sensors described in the literature perform admirably in lab settings, they utterly fall short when used in point-of-care (POC) applications. Non-specific adsorption on surfaces can be prevented by the creation of novel surface modification techniques. (iii) The need for field and point-of-care testing necessitates the development of miniaturized biosensors to increase portability. (iv) A highly automated and integrated optical sensor is ideal. Lab-on-a-chip (micro fluidics) sensors can also be made to rapidly find targets molecules. The real use of nanomaterial-based CL is still very limited. This research is expected to serve as a resource for the current and increasing application of various CL in the area of chemical and environmental analysis.

#### CRediT authorship contribution statement

**Simon Deepa:** Conceptualization, Investigation, Writing – original draft. **Raja Venkatesan:** Investigation, Formal analysis, Methodology, Writing – original draft. **Suseela Jayalakshmi:** Resources, Data curation. **Monogar Priya:** Visualization, Conceptualization. **Seong-Cheol Kim:** Supervision, Project administration, Funding acquisition, Writing – review & editing. All authors read and approved the final manuscript.

#### Declaration of Competing Interest

The authors declare no competing interests.

#### Data Availability

Data will be made available on request.

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