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Ultra-Weak Chemiluminescence

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Preface

Chemiluminescence involves chemical reactions which produce electronically excited states in sufficient quantity, and sufficiently quickly, to allow the occurring of the emission of light. It is concerned primarily with the emission of visible or near-visible radiation. Thus, chemiluminescence can be visible and bright, visible and dim, or invisible and ultra-weak. They can occur in gases, in liquids, and at the interface between solids and either a gas or liquid phase. Now many hundreds of organic and inorganic chemical reactions have been discovered which produce visible light. However, little works have been done on the ultra-weak chemiluminescence from inorganic chemical reactions.

We began to do research in developing new chemiluminescence systems and making apparatus for chemiluminescence detection since 1990s. During the past 30 years, our research group has made a great progress in principles and application of chemiluminescence, especially on the promotion of industrialization of chemiluminescence immunoassay technology. Chemiluminescence is a highly sensitive and most useful analytical technique, and is of great important in many fields, because of its low background interference and simple instrumentation. From the year's cooperation with enterprises, we find the education of basic knowledge of chemiluminescence is essential for the promotion of this technology. More than ten years ago, we have published two books in about chemiluminescence in Chinese language, such as Chemiluminescence-Basic Principles (Beijing Chemical Press, 2004) and Applications and Chemiluminescence Immunoassay (Beijing Chemical Press, 2008). Now, we are very pleased to do the further introduction of ultra-weak chemiluminescence combining the series research results of our group. We hope it will be helpful to the world's research and application of chemiluminescence.

This book is about the ultra-weak chemiluminescence. The emission of light caused by a chemical reaction is invisible to the naked eye but detectable by a sensitive photomultiplier tube. Recently, the ultra-weak chemiluminescence has had an impact on chemistry, on cell biology, and on biochemical and environmental analysis. Many of our cells are capable of producing an ultra-weak chemiluminescence spontaneously. The emission of a weak chemiluminescence from cells in the plant and animal kingdom during mitosis in ultraviolet region now has been observed.

Red ultra-weak chemiluminescence has even been detected in human breath. The reactions responsible for this invisible ultra-weak chemiluminescence are oxidation involving oxygen, oxygen metabolites, and radicals.

The inorganic elements which can participate in ultra-weak chemiluminescent reactions range from the alkali metals and heavy metals such as mercury and lead, to non-metals such as O, S, N, P, As, and the halogens. Compounds such as sulfate or sulfite, carbonate or bicarbonate, nitrite, and periodate would produce ultra-weak chemiluminescence when they coexisted with hydrogen peroxide in solutions. Research of these chemiluminescence mechanisms did great help for the explanation of most luminescent phenomena in nature and the understanding of the interaction of compounds containing carbon, nitrogen, sulfur, oxygen, halogen, and other elements, such as CO_2, CO_3^{2-}, HCO_3^-, NO_2^-, NO_2, NO_3^-, SO_2, SO_3^{2-}, IO_4^-, H_2O_2, and O_2. Compounds of silicon, the next element to carbon in group IV of the periodic table, also can produce chemiluminescence. Ultra-weak chemiluminescence is also responsible for light emission in many flames including those of N_2O, H_2S, CS_2, CO, and CN in air or oxygen. The ultra-weak red flash from the addition of H_2O_2 to sodium hypochlorite (NaClO), observed firstly by Mulliken in 1928, now has been known to be caused by singlet oxygen.

This book describes the study method of ultra-weak chemiluminescence providing many new technologies and new principles. Ultra-weak chemiluminescence in aqueous phase system is generated mainly by redox reactions with proper chemiluminescent reagents. To the inorganic ultra-weak chemiluminescence, the low intensity of these luminescence phenomena is because of a low overall quantum yield, or because of a low rate of reaction and/or the concentration of the chemiluminescent components is too low to generate a visible, functional light emission. The ultra-weak chemiluminescence can be induced or enhanced by addition of a variety of compounds. These compounds may themselves be chemiluminescent, or they may act on the pathway required to generate the endogenous ultra-weak chemiluminescence. For example, polycyclic aromatic hydrocarbon can enhance the ultra-weak chemiluminescence from the reaction of sodium hydrosulfite ($NaHSO_3$) with H_2O_2 by forming a new emitter from the radical reduction reaction. The enhancers fall into three broad categories: provision of chemiluminescent substrate, provision of oxidant, such as a hydroperoxide, and the energy transfer acceptors.

In recent years, great progress in ultra-weak chemiluminescence field has occurred, thanks to the development of new chemical probes, enhancers, and advanced instrumentation for light measurement and imaging. Specially, with the fast development of nanotechnology, many new nanomaterials have been applied in the ultra-weak chemiluminescence system to enhance the chemiluminescence intensity for further application. The cadmium series quantum dots, metal nanoalloys, carbon nanodots, and rare-earth-doped nanoparticles have been used to enhance the ultra-weak chemiluminescence from the decomposition of peroxymonocarbonate, peroxomonosulfite, and peroxynitrous acid, respectively. The enhanced chemiluminescence can be realized through a redox reaction by forming electron- and hole-injected nanoparticles. Metal surface plasmons also can enhance ultra-weak chemiluminescence by the chemically induced electronic excited states coupling to

surface plasmons. The surface plasmons-assisted metal catalysis process has been observed in the copper/nickel nanocomposite-enhanced ultra-weak chemiluminescence arising from peroxymonocarbonate. Energy transfer through electrons and radical annihilation is also involved in many well-known ultra-weak chemiluminescence reactions. The color of the emission is dependent on the fluorescent acceptor. The non-radiative energy transfer occurs only over very short distances of <0.1 nm, whereas others occur over distances as long as 10 nm. The result is a change in quantum yield, color, and sometimes rate of reaction.

The aim of this book is to provide a wide, but balanced, perspective on chemical reactions which produce ultra-weak chemiluminescence. The content includes fifteen chapters: what is so special about an ultra-weak chemiluminescence (Chap. 1), where they can be found (Chaps. 2–5), the kinds of active oxygen species in ultra-weak chemiluminescence (Chaps. 6 and 7), and ultra-weak chemiluminescence enhanced by functional materials (Chaps. 8–11). We attempted to highlight the unique aspects of ultra-weak chemiluminescence in analysis and to pinpoint where real discoveries have arisen from its use in chemistry, biology, medicine, environment, and forensic science.

The book is aimed at researchers and undergraduates in chemistry, physics, and biology. It describes particularly my own enthusiasm for studying ultra-weak chemiluminescence. We have deliberately repeated a few points in more than one chapter, so that each chapter may be read independently. It is our wish to encourage more people to discover more about this most exciting useful technique.

I would like to express my thanks to collaborators and colleagues too numerous to mention and also to many of my postgraduates.

December 2021   Jin-Ming Lin
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Contents

Chapter 1
Introduction of Ultra-Weak Chemiluminescence

Xiangnan Dou, Syed Niaz Ali Shah, and Jin-Ming Lin

Abstract This chapter gives an overview of the basic principle of chemiluminescence and ultra-weak chemiluminescence. The development of various ultra-weak CL systems will be introduced. The ultra-weak chemiluminescence based on reactive oxygen species will be focused in this chapter. Ultra-weak chemiluminescence hinders its application in analytical chemistry due to its low luminous efficiency. The roles of nanoparticles in enhancing these ultra-weak CL systems will also be reviewed.

Keywords Chemiluminescence · Ultra-weak chemiluminescence · Principle · Application

1.1 Introduction

Chemiluminescence (CL) is light emitted from a chemical reaction. The requirements for chemiluminescence are (1) The chemical reaction must provide enough excitation energy to enable the electron to transition from the ground state to the excited state, and (2) The energy from the chemical reaction can be accepted by at least one substance and generate an excited state; (3) the electronically excited products have chemiluminescence quantum yield to release photon or transfer its energy to other luminophores [1]. CL is typically observed during redox reaction processes. The chemiluminescence quantum yield, Φ_{CL}, is determined by the efficiency of generating the excited state product and the efficiency of an emitted photon of the excited state product. Φ_{CL} does not usually surpass 0.1–0.001% in most circumstances. Only a few CL systems, such as the unique substituted oxiamide or dioxetane intermediate, may achieve a yield of 30% [2]. High quantum yields ranging from 1 to 100% of luminescence emerges during oxidation of the luciferin, mediated by the enzyme luciferase in living cells. Luciferin and luciferase are substrates and enzymes that interact to produce visible light. It is the enzyme with a unique microenvironment and

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reactive properties that are frequently used as a reaction medium in bioluminescence. The quantum yields of the excited state species and emission in bioluminescent emission based on an enzymatic reaction are quite high. This means that some ultra-weak CL systems could be produced as CL reaction media, the quantum yield of CL may be improved.

The CL technique has the advantage of having mild response conditions and being simple to manage. CL provides several distinct advantages as an analytical method:

(1) Unlike fluorescence and UV–visible analysis, CL does not require an external light source, making it simple to integrate with other equipment like chromatography and capillary electrophoresis.
(2) The sensitivity of CL analysis is very high. CL excitation energy derives from chemical reactions (mostly redox reactions). As a result, CL analysis lowers the signal's effect on the source stability by eliminating Rayleigh and Raman scattering. A low level of noise and a high signal-to-noise ratio is achieved by the CL method, which has a detection limit as low as attomole (10^{-18}) or even zeptomole (10^{-21}).
(3) CL analysis may be used to detect substances involved in CL processes, including CL substrates, catalysts, inhibitors, and sensitizers.

During the last 40 years, many analysts have become interested in CL analysis because of its great sensitivity and ease of instrumentation. In contrast to the fluorescence approach, the exciting light source for CL is not required. As a result, the CL has found widespread application in clinical chemistry, biochemistry, and environmental chemistry, etc. The most evident manifestation of the rapid development is the large number of articles devoted solely to CL [3–10]. Because of its extraordinarily high sensitivity and other advantages, analytical methods comprising CL have recently attracted a lot of interest in a variety of sectors. Luminol, lucigenin, and oxalate esters are common CL systems [10, 11]. The CL method's exceptional sensitivity, however, presented a selectivity problem. Although various new CL systems are being developed for the identification of analytes [12–15], most CL systems could not be employed to directly determine the analytes. These limited CL systems only meet the needs of researchers for practical application. It's worth noting that the scarcity of functional CL systems is a key roadblock to CL's mainstream adoption. The quest for a new CL system is critical for expanding the scope of CL methods. Taking note of the fact that many redox reactions generate relatively faint light, the efforts on finding new CL systems is the main focus. The introduction of sensitizers or catalysts has already been shown to dramatically improve the CL properties of such weak CL systems [16, 17].

Many analysts worked hard to increase the CL intensity as well as the selectivity. Many new CL systems, both homogeneous and heterogeneous, have been created because of their work.

1.2 Principle of Chemiluminescence

CL can be produced by a chemical reaction that releases between 41 and 72 kcal per mole energy on its way to the product [18, 19]. There are three primary phases in the CL response. The first is the production of an intermediate that can react to provide enough energy to emit a visible light photon. The development of an electrically excited state is the next step. The CL reactions are distinguished from the rest of the chemical reactions by this step. The excited state's emission of light is the final stage [19]. The molecule's vibrational and rotational shifts are frequently accompanied by the electronic transition. Transitions from π bonding to π^* anti-bonding orbital $(\pi - \pi^*)$ or from a non-bonding to an anti-bonding orbital $(n - \pi^*)$ are the most common in organic compounds. CL denotes the return of an electron to its ground state accompanied by the emission of a photon. Excited molecules can also lose energy through a variety of mechanisms including chemical processes, collisional deactivation, internal conversion, and inter-system crossing. As a result, when these radiationless processes compete with CL, they are considered undesirable from an analytical perspective. The chemical interaction between the molecules A and B, as well as the energy transfer during the reaction, is depicted in Fig. 1.1.

In the first step, the reaction of A and B forms an excited state compound (C^*) which has a quantum yield Φ_{EX}.

$$A + B \xrightarrow{\text{Energy transfer}} C* \tag{1.1}$$

We can see from Fig. 1.1 that the excited molecule (C^*) can emit CL in two different ways.

(1) In the first case, C^* is a luminescence emitter that may be viewed through the luminescence emission.
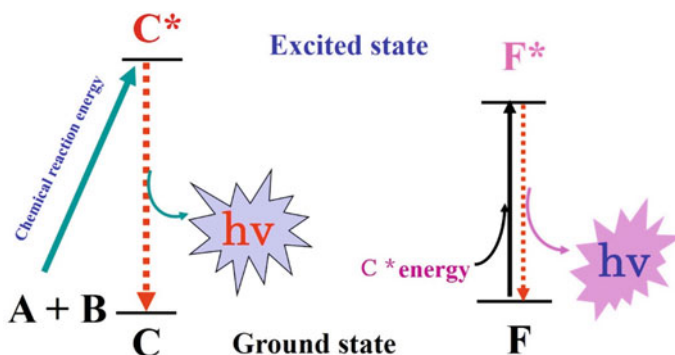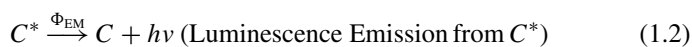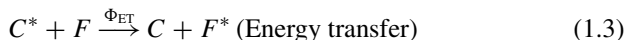
$$C* \xrightarrow{\Phi_{EM}} C + h\nu \text{ (Luminescence Emission from } C^*) \tag{1.2}$$

Fig. 1.1 The basic principle of chemiluminescence

(2) When the excited molecule C^* transferred its energy to the fluorescent
     molecule (F), the emission was increased by a more sensitive fluorescence.
     As a result, F is referred to as a CL enhancer, and the process is referred to as
     an enhancement CL reaction.

$$C^* + F \xrightarrow{\Phi_{ET}} C + F^* \text{ (Energy transfer)} \quad (1.3)$$

$$F^* \xrightarrow{\Phi_F} F + h\nu \text{ (Fluorescence Emission from } F^*) \quad (1.4)$$

As soon as the CL reaction was initiated in the first instance. The quantum yield
(CL) is the fraction of molecules that produce a photon when they return to their
ground state. It is calculated as the product of two ratios:

$$\Phi_{CL} = \Phi_{EX} \cdot \Phi_{EM} \quad (1.5)$$

Traditional CL systems often have very poor quantum yields, either because of
heat release or because of quenching from the surrounding environment. To avoid
this difficulty, it is recommended that a fluorescent chemical with a reasonably high
quantum yield be added to the reaction mixture to facilitate the transfer of energy to
the fluorescent species [18]. As its name implies, this type of CL system emits its
ultimate emission from an excited state created by direct oxidation of the excitation
step. It is referred to as the direct CL system. The indirect CL system, on the other
hand, is a CL system in which the final emission occurs indirectly because of energy
transfer from the first created excited state, as opposed to the direct CL system [19].
Recently, nanomaterials (NMs) have been widely used to increase the CL intensity
of classical systems, which is a significant advancement.

Inorganic reactions in CL systems produce weak CL emissions because of the
low quantum yield of the inorganic reactions. For analytical applications, then, it is
important to increase the CL intensity level. Compounds such as NMs, transition
elements, and/or reaction techniques such as catalytic and energy transfer processes
have been proposed to improve the CL signals of these compounds [20]. Currently,
there is a considerable deal of interest in CL signal enhancement [21]. The research
orientation in CL is partially devoted to the development of novel CL systems and
partly to the application of these systems to real samples, with the former being the
primary focus. This type of research can be primarily focused on discovering new
CL reagents, such as substrates, sensitizers, and catalysts [22].

In general, the CL reaction is a redox reaction [23], which involves the partic-
ipation of a variety of reactive oxygen species (ROS) [24, 25]. Hydroxyl radical
($^\bullet$OH), superoxide radical ($^\bullet O_2^-$), and substrate radicals, as well as singlet oxygen
($^1O_2$), are all examples of ROS [24–26]. Increased ROS generation is a frequently
used technique for increasing the CL intensity of a system [27]. The peroxide-
induced CL systems have garnered considerable attention and are widely used in
a variety of fields. Hydrogen peroxide (H_2O_2), peroxymonocarbonate, peroxysul-
fite, and peroxynitrite are all examples of peroxides [28]. H_2O_2 has a critical role

in the CL responses [23]. The breakdown of H_2O_2 in a CL reaction generates reactive oxygen species (ROS) [13, 29]. Many CL emissions from a system are possible because of the system's multiple CL paths. Multiple CL pathways can occur concurrently in the same system. The quenching of CL signals occurs when a CL pathway is blocked. CL emission may have increased because of the closure of a less efficient CL pathway [24]. To detect and track these radicals in a CL system, electron paramagnetic resonance (EPR) and free radical scavengers are utilized.

1.3 Development of Ultra-Weak CL Systems

CL provides several advantages for analytical chemistry applications, including high sensitivity, a broad linear range, simple and inexpensive apparatus, and minimal background noise. However, many CL systems use certain conventional reagents, including luminol, lucigenin, acridinium, AMPPD, and $Ru(bpy)_3^{2+}$, the majority of which are organic molecules. We have attempted to build various new CL systems based on inorganic reactions throughout the last two decades, notwithstanding the difficulty of directly detecting light emissions using CL approaches due to the poor quantum yield. The book focuses on the construction of ultra-weak CL systems using peroxymonocarbonate, peroxynitrous/peroxynitrite, peroxysulfite, periodate, or hydrogen peroxide as starting materials. Additionally, it will address ultra-weak CL that has been boosted or amplified by nanoparticles, quantum dots, or layered double hydroxide (LDH), as well as aggregation-induced emission (AIE).
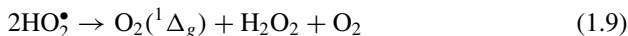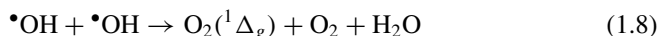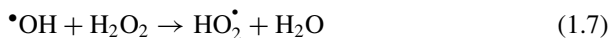
1.3.1 Hydrogen Peroxide-Based Chemiluminescence

1.3.1.1 Fenton/Fenton like System

The Fenton reaction, which produces hydroxyl radicals, is commonly utilized in the practice of scientific research as a source of radicals. It is the Fenton reaction that produces the light radiation that may be measured by a contemporary luminometer. The metal (M)-catalyzed breakdown of H_2O_2 results in the formation of the $^\bullet$OH radical [30].

$$H_2O_2 + M^n \rightarrow M^{n+1} + {}^\bullet OH + {}^- OH \tag{1.6}$$
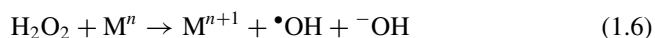
Initially, the Fenton reaction resulted in the creation of reactive oxygen species (ROS), which then resulted in the emission of CL. When the Fenton reagent is introduced, a flash of light can be seen. The singlet oxygen ($^1O_2$) is the emissive species that emits luminescence. The following is an example of the ROS production response resulting from the Fenton reaction [31]. Lin et al. used CDs for the enhancement of the Fenton system [32, 33].

$$\text{}^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{1.7}$$

$$\text{}^\bullet OH + \text{}^\bullet OH \rightarrow O_2(^1\Delta_g) + O_2 + H_2O \tag{1.8}$$

$$2HO_2^\bullet \rightarrow O_2(^1\Delta_g) + H_2O_2 + O_2 \tag{1.9}$$

1.3.1.2 Peroxynitrite (ONOO⁻) CL System

Peroxynitrite (ONOO⁻) is a substantial nitric oxide derivative that has a wide range of uses in several fields. Even though peroxynitrite has a half-life of 10–20 ms, it is sufficiently stable to permeate biological membranes, diffuse one to two cell diameters, and interact with many essential biomolecules [34].

The coupling of $NO^\bullet$ and $^\bullet O_2^-$ radicals in biological systems is most likely the source of ONOO⁻ (Eq. 1.10) [35]. Furthermore, ONOO⁻ can be produced by mixing acidified H_2O_2 with nitrite in real-time. Nitrite reacts with hydrogen peroxide in an acidic medium to form ONOOH (Eq. 1.11), which is unstable and can be decomposed into ONOO⁻. Weak chemiluminescence was observed during the decomposition of ONOO⁻.

$$^\bullet O_2^- + NO^\bullet \rightarrow ONOO^- \tag{1.10}$$

$$H_2O_2 + HNO_2 \rightarrow ONOOH + H_2O \tag{1.11}$$

$$^-OH + ONOOH \rightarrow ONOO^- + H_2O \tag{1.12}$$
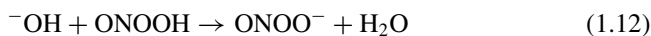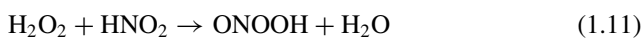
Several studies described how fluorescent compounds and NMs such as CdTe QDs, Mg–Al carbonate LDHs, CDs, and Au NPs improve the CL from ONOO⁻ [36–38]. Carbonate has been shown to react with ONOO⁻ to form the adduct $ONOOCO_2^-$, which decomposes fast into $^\bullet NO_2$ and the carbonate radical ($CO_3^{\bullet-}$), according to the literature. It is the conversion of the $CO_3^{\bullet-}$ radical into CO_2 in its excited form that causes the CL emission. CDs were shown to significantly increase the CL from the peroxynitrous acid (ONOOH) and CO_3^{2-} CL system described by Lin et al. [39] (Fig. 1.2).

1.3.1.3 Peroxysulfite (HSO₄⁻) CL System

Early in the twentieth century, the H_2O_2–HSO_3^- CL phenomena were identified by Stauff [40]. A peroxysulfite compound (HSO_4^- or $HOOSO_2^-$) is generated during the interaction of HSO_3^- with hydrogen peroxide. This compound is unstable and can be converted into the radicals $^\bullet SO_3^-$ and $^\bullet OH$ in the presence of H_2O_2. There
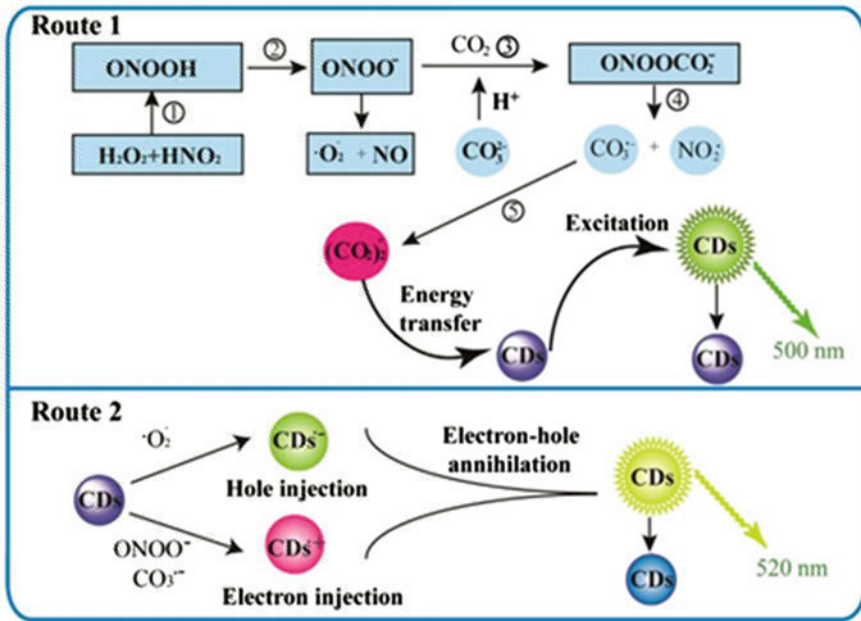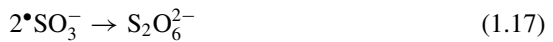
Fig. 1.2 Schematic of the CL process in the carbon nanodots–NaNO$_2$–H$_2$O$_2$–Na$_2$CO$_3$ system using a schematic diagram [39]

are many CL emitting molecules, such as SO$_2$* and ^{1}O$_2$ that have been produced through radical reactions [41, 42].

$$H_2O_2 + HSO_3^- \rightarrow HOOSO_2^- + H_2O \tag{1.13}$$

$$HOOSO_2^- \rightarrow {}^\bullet OH + {}^\bullet SO_3^- \tag{1.14}$$

$$2HO_2^\bullet \rightarrow {}^1O_2 + H_2O_2 \tag{1.15}$$

$$HSO_3^- + {}^\bullet OH \rightarrow {}^\bullet SO_3^- + H_2O \tag{1.16}$$

$$2{}^\bullet SO_3^- \rightarrow S_2O_6^{2-} \tag{1.17}$$

$$S_2O_6^{2-} \rightarrow SO_2^* + SO_4^{2-} \tag{1.18}$$

$$SO_2^* \rightarrow SO_2 + h\nu \tag{1.19}$$
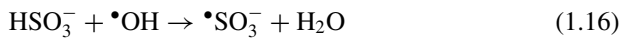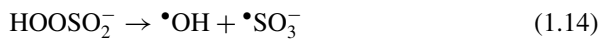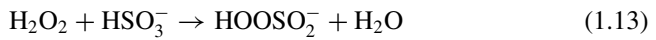
Xue et al. investigated the influence of CDs on the H_2O_2–HSO_3^- CL system and discovered that they had an enhanced effect [43]. In the H_2O_2–$NaHSO_3$ system, the CDs aided in the production of the emitter species SO_2* and $^1O_2$ by facilitating the creation of these species (Fig. 1.3a). The CL of the H_2O_2–$NaHSO_3$ system was also improved using plasmonic luminous core–shell nanocomposites. According to [44], the combination of chemically produced excited states with surface plasmons results in an amplifying effect (Fig. 1.3b).

As a result of its high oxidation potential and proclivity to react through oxygen transfer, peroxysulfite (HSO_4^-) is one of the most promising oxidants for organic molecules in use today. Comparative to other common reagents such as peroxodisulphate and peroxomonophosphoric acid, it has also been shown to be a powerful oxidizing agent. Chaps. 5 and 6 will discuss the CL of HSO_4^- in further detail.
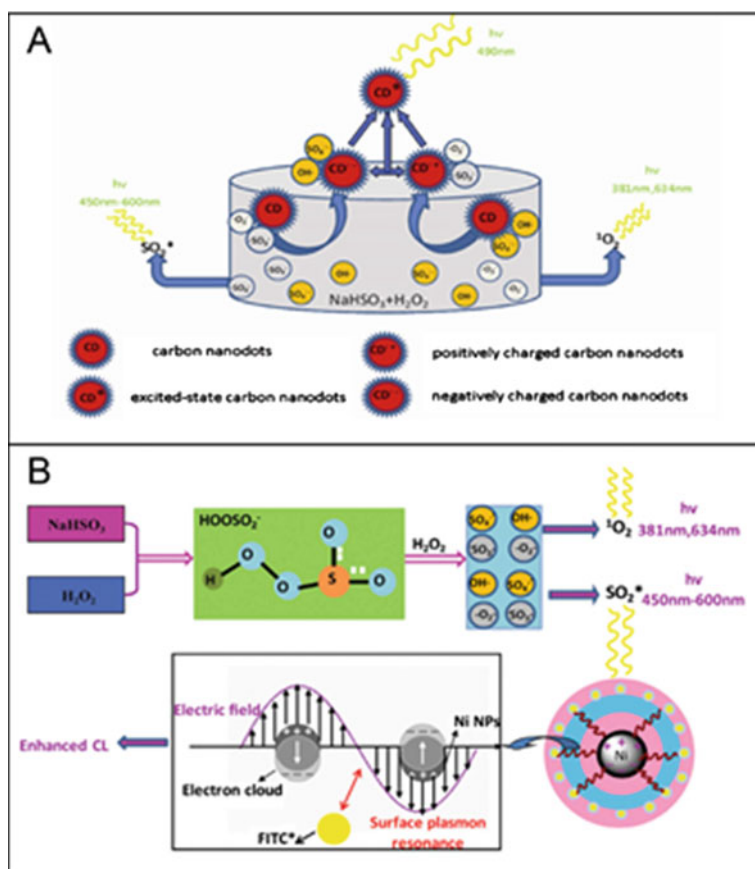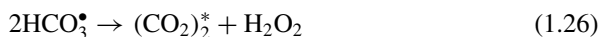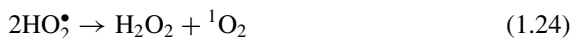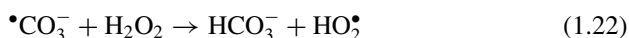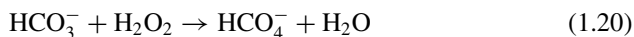

Fig. 1.3 a The mechanism of the CL reaction in the H_2O_2–$NaHSO_3$ CDs system [43]; **b** the enhancement of CL intensity from the H_2O_2–$NaHSO_3$ system by plasmonic luminous nanocomposites [44]

1.3.1.4 Peroxymonocarbonate CL System

Peroxymonocarbonate (HCO_4^-) has been reported as a product of the interaction of hydrogen peroxide with bicarbonate since the 1980s. The breakdown of HCO_4^- resulted in the formation of CL. Carbonate radical was created as a result of it. The CL emitters includes singlet oxygen ($^1O_2$), singlet oxygen molecular pair [$(O_2)_2$*], and excited double $(CO_2)_2$*.

$$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O \qquad (1.20)$$

$$HCO_4^- \rightarrow {}^\bullet OH + {}^\bullet CO_3^- \qquad (1.21)$$

$${}^\bullet CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2^\bullet \qquad (1.22)$$

$$HO_2^\bullet \rightarrow {}^\bullet O_2^- + H^+ \qquad (1.23)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + {}^1O_2 \qquad (1.24)$$

$$4^\bullet O_2^- + 4H_2O \rightarrow (O_2)_2^* + 4^-OH + 2H_2O_2 \qquad (1.25)$$

$$2HCO_3^\bullet \rightarrow (CO_2)_2^* + H_2O_2 \qquad (1.26)$$

Many articles are focused on improving the peroxymonocarbonate system's ultra-weak CL. Cu/Ni metal NPs were used to increase the ultra-weak CL utilizing surface plasmons [45]. Protein-stabilized zinc/copper nanoclusters have been shown to greatly increase the CL of peroxymonocarbonate [46]. The catalysis of Zn/Cu@BSA nanoclusters and the metal surface plasmon-linked emission of excited $(CO_2)_2$* resulted in the enhanced CL.

1.3.1.5 Periodate CL System

The periodate produces soft oxidation products and has been used for the microanalysis of different compounds [18, 47]. The periodate reacts with H_2O_2 in acidic, neutral, and basic mediums to produce $^1O_2$ as an emissive species [48]. Various researchers used different enhancers to amplify the CL intensity of this system [49]. Lin et al. [50] used sodium dodecylbenzene sulfonate (SDBS) modified layered double hydroxides to enhance the CL intensity of the IO_4^-–H_2O_2 system (Fig. 1.4a). Our group used nitrogen-doped CDs for the enhancement of this system [51, 52]. Shah et al. [53] reviewed the details on the improvement and application of the periodate-peroxide CL system recently.
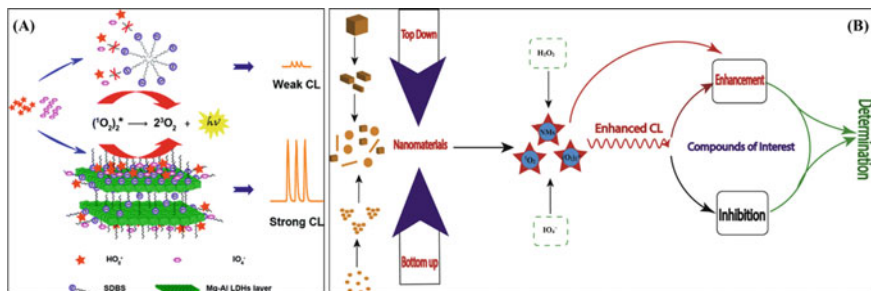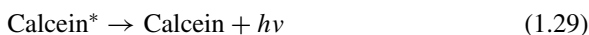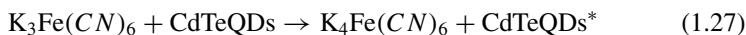
Fig. 1.4 a The mechanism of CL enhancement by sodium dodecylbenzene sulfonate (SDBS)-modified LDHs [50]. **b** Detailed about the improvement and application of the periodate-peroxide CL system [53]

1.3.2 The Role of NPs in the CL System

Because of their possible application in CL, nanomaterials (NMs) with good optical and electrical characteristics have gotten a lot of attention. Many studies have attempted to employ nanoparticles (NPs) to boost CL in various ultra-weak CL systems, including H_2O_2–$NaHCO_3$, H_2O_2–$NaIO_4$, H_2O_2–$NaNO_2$, H_2O_2–$NaClO$, H_2O_2–$NaHSO_3$, and others [52, 54, 55]. NPs can directly participate in redox reactions or operate as catalysts or energy acceptors in CL processes, to boost CL intensity. The role of NPs in the CL system is summarized below.

1.3.2.1 Direct CL

Excitons being a bound state of the introduced electrons and holes in the conduction and valence bands of the nanomaterials, respectively, is usually generated during a CL reaction involving nanomaterials. The relaxation of excitons resulted in the NPs-based CL. The CL system of CdTe QDs–calcein–$K_3Fe(CN)_6$ was developed by Zhang et al. [56], in which CdTe QDs directly participating in the reaction by oxidized to excited CdTe QDs by $K_3Fe(CN)_6$. The excited CdTe QDs are capable of transferring their energy to the calcein acceptor through a process known as energy transfer.

$$K_3Fe(CN)_6 + CdTeQDs \rightarrow K_4Fe(CN)_6 + CdTeQDs^* \tag{1.27}$$

$$CdTeQDs^* + Calcein \rightarrow CdTeQDs + Calcein^* \tag{1.28}$$

$$Calcein^* \rightarrow Calcein + h\nu \tag{1.29}$$

Lin et al. discovered carbon dots could react with acidic $KMnO_4$ and cerium (IV) to emit CL [57]. Such oxidants could cause holes to form in the CDs. The injection of holes into carbon dots by an oxidant increases the number of holes in the CDs and speeds up electron–hole annihilation, resulting in energy release in the form of CL emission.

Li et al. [58] discovered that CdTe/CdS/ZnS QDs exhibit novel CL performance with KIO_4. The direct oxidation of CdTe/CdS/ZnS QDs by dissolved O_2 produced a superoxide radical ($^\bullet O_2^-$), $QD(e_{1se}^-)$ and $QD(h_{1sh}^+)$ excitons were generated by injecting electrons and holes from $^\bullet O_2^-$ and $^\bullet OH$ radicals, respectively, resulting in QDs* in the excited state.

$$QD + O_2 \rightarrow {}^\bullet O_2^- + QD^{+\bullet} \tag{1.30}$$

$$2{}^\bullet O_2^- + 2H_2O \rightarrow {}^1O_2 + 2{}^-OH + H_2O_2 \tag{1.31}$$

$$^\bullet O_2^- + H_2O_2 \rightarrow {}^-OH + {}^\bullet OH + O_2 \tag{1.32}$$

$$QD + {}^\bullet O_2^- \rightarrow O_2 + QD(e_{1se}^-) \tag{1.33}$$

$$QD + {}^\bullet OH \rightarrow {}^-OH + QD(h_{1sh}^+) \tag{1.34}$$

$$QD(e_{1se}^-) + QD(h_{1sh}^+) \rightarrow QD^* \tag{1.35}$$

$$QD^* \rightarrow QD + h\nu \tag{1.36}$$
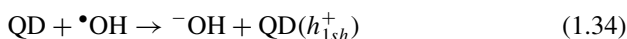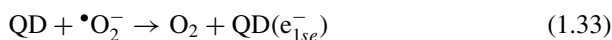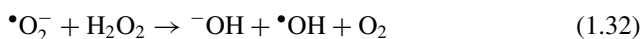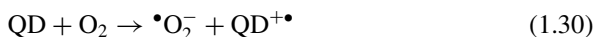
1.3.2.2 CL Catalyst

Many research groups have investigated the catalytic effect of NMs. The NMs-based catalytic CL system was developed as an analytical chemical sensor. The catalytic effect or enhancement of CL processes by NMs is attributed to the formation of reactive oxygen radicals such as $^\bullet OH$ radical, and $^\bullet O_2^-$ radical, which are initiated by catalysts or enhancers. The NMs, particularly those containing transition metals, exhibit a significant catalytic outcome on H_2O_2-based CL systems, such as luminol–H_2O_2 and lucigenin–H_2O_2.

Furthermore, CL responses varied depending on the morphology and composition of catalytic NMs. Take, for example, the work of Li et al. [59], who investigated the CL response of triangular Au NPs in the luminol–H_2O_2 system and contrasted it with the reaction of spherical Au NPs. According to the researchers, when compared to spherical Au NPs, triangular Au NPs exhibited much higher catalytic activity due to a higher surface-to-volume ratio and a greater number of active surface sites. These

triangular Au NPs exhibited improved activity in the formation of reactive oxygen radicals and electron transferability on their surfaces. It has also been demonstrated that the CL system of luminol–H_2O_2 catalyzed by triangular Au NPs has excellent analytical application for the detection of aminothiols.

Because of the redox feature of the distinct electron and hole states of QDs, they can act as a catalyst in CL systems. With QDs, the injection of holes from a strong oxidizer or electrons from a reducer can alter the valence and conduction bands of the QDs. During the injection procedure, ROS such as $^\bullet OH$, $^\bullet O_2^-$ radicals will be created. By radical reactions, these radical species can oxidize CL reagents, resulting in increased CL, or generating CL emitters. L-cysteine capped Mn-doped ZnS QDs have previously been shown to improve CL of the H_2O_2-NaClO system [60]. The increased CL of NaClO–H_2O_2 is due to the sensitizer's catalysis in creating reactive intermediates as well as the electron-transfer mechanism [53].

The CL's efficiencies were affected by the types of reactants and catalysts used. Chen et al. [61] demonstrated improved CL of the H_2O_2–$NaHCO_3$ system with the addition of CdTe QDs. The excited CdTe QDs were produced by combining the hole and electron injected QDs, which cause the enhancement of CL. They investigated the size effect of various catalyst types on the CL of the H_2O_2–$NaHCO_3$ system. CdTe QDs were compared to CdSe and CdS QDs with emission wavelengths of 549 and 607 nm, respectively. They discovered that CdTe QDs with a larger size than CdSe and CdS quantum dots at the same concentration could significantly increase CL intensity.

1.4   Conclusion

The purpose of this chapter is to introduce the basic principles of chemiluminescence and the development of ultra-weak CL systems, focusing on the CL from the decomposition of peroxynitrite ($ONOO^-$), peroxymonocarbonate (HCO_4^-), peroxysulfite (HSO_4^-), and periodate (IO_4^-), as well as the application of NPs to develop new reactive oxygen (ROS) CL systems and enhance the weak CL systems. More information on the CL of these inorganic compounds can be found in Chaps. 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 of this book.

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