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## Review

## Dendrimers: New tool for enhancement of electrochemiluminescent signal

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## ABSTRACT

Electrochemiluminescence or Electrogenerated chemiluminescence (ECL) is a powerful analytical technique combining excellent features of an electrochemical and luminescent method. The process involves generation of an electro-active species due to the electron transfer reactions (redox-reactions) at an electrode surfaces to form excited states, which on relaxation emits light. ECL as a technique has received great attention in biosensing due to its high sensitivity and ability to detect wide range of analytes. This review presents the analytical importance of electrochemiluminescence (ECL)-based detection methods. The mechanism of ECL detection is briefly presented. Why there is a need to enhance the ECL signal in biosensing is discussed and the nanomaterials which are presently reported to enhance the ECL signal are reviewed. Among various nanomaterials, dendrimers as tools for enhancing the ECL signal is explored and reviewed in detail. Finally, challenges and perspectives of the use of dendrimers in ECL are discussed.

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## 1. Introduction

In recent times, electrochemiluminescence (ECL), also known as electrogenerated chemiluminescence, has become an important analytical detection technique which involves emission of light by relaxation of excited state molecules produced during an electrochemical reaction [1]. In ECL, there is no need of an excitation light source that produces background signals and scattering and therefore this technique is aptly suitable for detection of analytes at low concentrations over a wide linear range without the use of any expensive instrumentation [2]. ECL has several advantages over conventional spectroscopic techniques. The significant one is that the ECL signal is produced only by concomitant electrochemical initiation reaction, which depends on the applied potential. This reaction when coupled with an optical fibre which is placed very close to the electrode surface, allows spatial and temporal control over the reaction with high selectivity and improved signal-to-noise ratio. Besides this, ECL has an edge over other electrochemical techniques due to the absence of electrical interferences. Additionally, in ECL, the reactive species can be immobilized and pre-concentrated on electrode surfaces thereby increasing the light

intensity and regeneration of the reactants at the electrode surface [2]. ECL finds its applications in wide variety of bioanalytical assays such as ECL immunoassays, ECL DNA probe assays, and recent trends being seen for the development of ECL biosensors.

Amongst several ECL producing reagents, inorganic complexes and organic molecule like ruthenium bipyridyl complexes, (Ru(bpy)<sub>3</sub>)<sup>2+</sup> [3] and luminol [4], respectively are used most commonly. Recently, CdSe and CdTe quantum dots (QDs) are also being explored as ECL reagents as they can emit light under application of suitable potential [5,6]. Polyaromatic hydrocarbons were also tried but could not be successfully used in chemical analysis due to their insolubility in aqueous solutions [7].

ECL-generating species are employed as labels on biological molecules allowing clinically relevant analytes to be detected at subpicomolar concentrations via conventional immunoassays or nucleic acid assay approaches [8]. However, for medical applications highly selective and sensitive detection plays a major role especially in the area of diagnostics. Thus, there is a demand to find a way or an alternative approach to enhance the ECL signal for sensitive detection. Active research is being carried out nowadays integrating nanomaterials that exhibit enhanced properties due to increased surface area, making them an ideal candidate for electroanalytical applications. Tremendous efforts are recently being carried out to find new co-reactants to improve ECL efficiencies.

In this review, we focus on dendrimers that could act as co-

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reactant in enhancing ECL signal. Dendrimers are a class of three-dimensional globular and symmetrical macromolecular which are known to enhance properties such as water solubility, chemical stability, surface functionality. On the other hand, they can behave as an excellent redox centers for energy-transfer reactions [9] which is a vital process in electrochemistry. With this review, we aim to provide a general overview of the latest developments in the area of ECL detection. The use of nanomaterials as co-reactant will be emphasized and discussed.

## 2. Recent development and basics of ECL

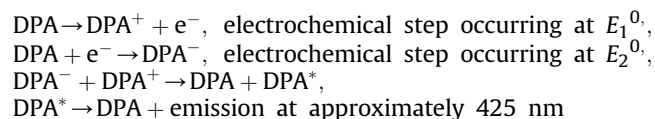
ECL is a means of converting electrical energy into radiative energy [10]. It involves electrochemistry exploiting redox-reactions to generate highly-reactive (intermediate) species and chemiluminescence that generates light which is initiated and controlled by changing an electrode potential. In addition to inorganic and organic molecular luminophores, nanomaterial systems such as quantum dots, metal nanocrystals, and carbon nanomaterials have recently aroused much research interest as ECL electrocatalysts and ECL emitters due to their special properties. A combination of traditional ECL agents with nanoparticles is a very promising way to develop new efficient luminophores. Liu et al. [11] has recently reviewed latest developments of ECL systems describing mechanistic approaches for wireless ECL devices, bipolar electrochemistry, resonance energy transfer ECL, and microfluidic ECL platform. Qi et al. [12] designed and reported the first study on wireless ECL device by employing a diode in an electrode array chip. The diode was embedded in an electromagnetic receiver coil and was utilized to rectify alternating current into direct current. The latest strategy could enhance ECL intensities by 18 thousand times enabling common cameras or smart phones as low cost detectors. The device was coupled with photomultiplier tube based detectors to detect luminol with high sensitivity and linear range from 10 nM to 1 mM. An impressive amount of research nowadays has also been focused on development of microfluidic based devices. Microfluidics offer obvious advantages in the reduced consumption of reagents: faster and more sensitive reactions due to enhanced effects of processes such as diffusion and mass transport; increased throughput through parallel processing; and reduced expenses in terms of power and reagent consumption [13]. Sardesai et al. [14] demonstrated microfluidic ECL device for sensitive detection of prostate specific antigen (PSA) and interleukin-6 (IL-6) in serum. This developed strategy achieved ultralow detection limits of 100 fg mL<sup>-1</sup> for PSA and 10 fg mL<sup>-1</sup> for IL-6 in calf serum which stated a 10–25 fold improvement of a similar non-microfluidic array. Kirschbaum et al. [15] has presented an excellent review on ECL for microfluidic analytical devices describing advanced ECL systems with goal of reaching lower limit of detection. Thus, recent developments are being seen for portable ECL devices desirable for point-of-care testing and field analysis.

The commercial systems are based on co-reactant ECL, but the earlier studies originated with ion-annihilation ECL. The ECL signals are produced by two major ways: the *ion annihilation* and the *co-reactant* pathways; and in both the pathways, two species are generated electrochemically which then undergo electron transfer reaction to produce a light emitting species. Most of the analytical applications are based on co-reactant pathways, hence will be discussed in detail in this review.

### 2.1. Ion-annihilation ECL pathway

The ion annihilation pathways involves formation of electrochemical intermediate species at the electrode surface which are annihilated by oppositely charged radical ions to form

electronically excited states of the compound that emits light upon relaxation [16]. Here, ECL involves electron-transfer reactions between an oxidized and reduced species, both of which are generated by alternate pulsing of the electrode potential. For example, the electrochemically generated anion and cation radicals of 9,10-diphenylanthracene (DPA) recombine to form one DPA (ground state) and one excited state DPA\*.



One of the criteria for efficient annihilation ECL is that both anion and cation radicals formed from the ECL precursor must be stable in the electrolyte of interest. Therefore, the annihilation pathway requires only the electrochemiluminescent species, solvent with wide potential window like acetonitrile and *N,N*-dimethylformamide, and supporting electrolyte to generate light. However, the major disadvantage observed for annihilation ECL is that the radical ions generated are chemically unstable and incapable of retaining their charges till it interacts with the oppositely charged ions. Another drawback of the ion-annihilation pathway is that water cannot be used as a solvent because the potential window of water is not sufficiently wide to allow the luminophore to be both oxidized and reduced [8].

### 2.2. Co-reactant ECL pathway

Co-reactant ECL pathway involves one-directional potential scanning of the solution containing a luminophore and a reagent (co-reactant) which can be easily oxidized or reduced on application of electrode potential. The co-reactant undergoes rapid chemical reaction to form an intermediate species with sufficient oxidizing or reducing power to excite the luminophore and produce subsequent ECL emission. In contrast to ion annihilation ECL, where all starting species can be regenerated after light emission, in a co-reactant ECL system, only luminophore can be regenerated; the co-reactant species is consumed during the electrochemical reaction. The main advantage of the co-reactant ECL is that they can be performed in aqueous solution which gives access to a wide range of biological assays and diagnostics. Thus, the majority of the commercial ECL analytical instruments are based on co-reactant pathway [2].

Several factors contribute to the selection of a good ECL co-reactant like solubility, stability, electrochemical properties, quenching effect, to mention a few. Commonly used ECL co-reactants are oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), tripropylamine (TPA), Peroxydisulfate (Persulfate, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), pyruvate etc.

The co-reactant ECL works in 4 steps: (i) redox reaction at the electrode, (ii) chemical reaction, (iii) generation of excited-state species, and (iv) emission of light. The redox reactions are either homogeneous or heterogeneous depending upon the redox potential of the co-reactant and the nature of the working electrode. Based on the generation of the intermediates, the ECL can be either “oxidative–reduction” when highly reducing intermediate species are generated after an electrochemical oxidation of a co-reactant, or “reductive–oxidation” where highly oxidizing intermediates are produced after an electrochemical reduction [17,18].

#### 2.2.1. Reductive–oxidation systems

Reductive–oxidation ECL is produced by applying a negative potential. Example of the system is Peroxydisulfate (Persulfate, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) co-reactant. Typically, the persulfate reacts with Ru(bpy)<sub>3</sub><sup>3+</sup> in a mixed solution of dimethylformamide (DMF)-water or

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