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Review

# Electrogenerated chemiluminescence from metal complexes-based nanoparticles for highly sensitive sensors applications

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ABSTRACT

The coupling of nanomaterials, and nanoparticles in particular, with one of the most powerful transduction techniques, electrochemiluminescence (ECL), i.e., chemiluminescence triggered by electrochemical reactions at electrodes, has recently provided sensing tools with unprecedented sensitivity limits. This review aims to give an overview of the state of the art in the field over the last 5 years, i.e., a time span covering over 80% of the scientific production in this context. The results herein discussed would demonstrate that the use of nanoparticles in the ECL technique represents one of the most interesting research lines for the development of ultrasensitive analytical tools, offering an insight to recognize and select the best nanomaterials for ECL signal amplification, with particular emphasis in biosensing.



**Contents**



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## 1. Introduction

The importance of nanotechnology and nanosystems on chemical and materials science has steadily been increasing over the last decade, with an ever-larger impact at any level in the development of new technologies [1]. In the field of analytical sciences, in particular, nanoparticles have been playing a unique role among other nanosystems, in bringing the sensitivity of sensing devices to their ultimate levels, providing, e.g., ultrabright labels in clinical analysis (markers, tumor cells, and pharmaceuticals) and in the detection of pathogenic microorganisms, toxic agents, and pesticides in the environmental field and food products [2,3]. Coupling such nanosystems with *electrochemiluminescence* (ECL), which naturally brings improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background, has brought about new systems and strategies for analytes determination, even in very complex matrices, such as urine, blood or lysate, thus finally shifting the detection levels from the ppm range to the ppb or pg $mL^{-1}$, so far achievable only by other, technologically more demanding techniques. By coupling nanomaterials with ECL, for example, has provided a rapid, cost-effective and ultrasensitive assay for the detection of Zika virus (ZIKV, emerging mosquito-transmitted flavivirus) that could be detected at levels as low as 1 virus particle in 100 μL of saline, human plasma, or human urine, a level which cannot be achieved by any other techniques [4].

In such a context, the results of a literature search carried out over the last decades, by combining the terms "nanoparticle" and "electrochemiluminescence", have shown an exponential increase of scientific production in the field especially in the last years, with over 80% of documents concentrated in the last 5 years. This would suggest therefore the necessity of an update of our previous review, published in this Journal in 2013 [5]. Herein, the most original and influential contributions within a huge variety of recent scientific production have been carefully selected to provide a timely and, hopefully, useful tool to all those who are either already active or just approaching such a fascinating research field.

### 1.1. Principles of electrogenerated chemiluminescence

*Electrogenerated chemiluminescence*, also *electrochemiluminescence* (ECL), is emission of photons from a molecular species (luminophore) following an electron transfer (ET) process in solution, triggered by an electrochemical reaction [6]. As a combination between electrochemical and photophysical methods, ECL shows several advantages over chemiluminescence (CL) and photoluminescence (PL), such as near zero background noise due to the absence of excitation light sources and superior temporal and spatial control on light emission. As a matter of fact, ECL has become a powerful analytical technique and has widely been applied in many fields including environmental investigations, bioanalysis and immunoassays [7–9].

The first appearance of this phenomenon can be traced back to 1920s, [10] but the beginning of this electrochemical technique, as it is known today, started in the 1960s from the pioneering works of Hercules, [11] Pragst, [12] Chandross [13] and Bard [14]. The story of ECL went rapidly from an academic curiosity to a powerful electroanalytical technique [7–8,15–16] and nowadays, the research on ECL is mainly focused on its analytical applications, mostly having important biological targets [9,17–21]. Although tris(2,2′-bipyridyl)ruthenium(II) $[Ru(bpy)_3^{2+}]$ still remains the benchmark, there is extensive research activity in developing new inorganic complexes, organometallic species or organic molecules for ECL, either freely diffusing in solution or embedded within nanosystems [5,22–24]. In this context, nanomaterials play a crucial role that ranges from the investigation of the complex mechanisms for ECL generation to the study of the electrochemical behavior of new high efficient dyes.

### 1.2. Fundamentals of electrogenerated chemiluminescence

In order to generate ECL, two species, an electron donor D and an electron acceptor A both produced at the electrode surface, may undergo an ET process with one another (in the diffusion layer) to obtain the excited state of one of them (the luminophore). The energy requirement is the first parameter to predict if the ECL emission will take place as the ET should provide enough energy for "energy sufficient" ECL. The energy involved in the ET can be expressed in term of formal potentials of the species:

$$-\Delta H^0 = E^\circ(D^{+\cdot}, D) - E^\circ(A, A^{-\cdot}) - T\Delta S^0 > \frac{1239.81}{\lambda_{es}(nm)} \quad (1)$$

where, $E^\circ(D^{+\cdot}, D)$ and $E^\circ(A, A^{-\cdot})$ are the standard potentials of the reacting species, and $\lambda_{es}$ is the excited state emission wavelength of the luminophore. The term $\Delta S^\circ$ arises from the Coulomb repulsion associated to bringing the reactants from infinite into the encounter complex, a term that is typically small ($\leq$0.1 eV) at 298 K [6]. A good approximation is therefore:

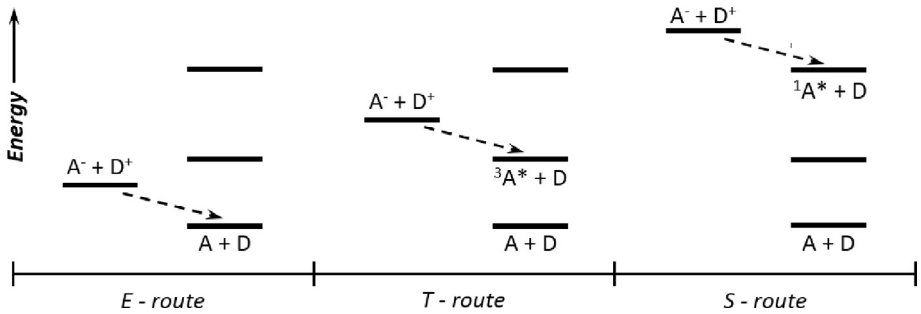


**Fig. 1.** Relation of ECL pathways to energy requirements (adapted from Ref. [6]).