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Review

Nanoparticles in metal complexes-based electrogenerated chemiluminescence for highly sensitive applications

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ABSTRACT

This review aims to give an overview on the state of the art in the precise context of metal complexes-based ECL dyes directly adsorbed on, included in or interacting with nanoparticles of various nature. Electrogenerated chemiluminescence, or electrochemiluminescence (ECL), is the process through which species generated at electrodes undergo homogeneous high-energy electron transfer reactions to give excited states that emit light. When stable ECL probes such as ruthenium coordination complexes are used, this process can be performed several times, free of the interferences typical of photoluminescence such as the excitation light, providing a clear and stable signal suitable for highly sensitive assays. The

Abbreviations: acac, acetylacetonate; ADH, alcohol dehydrogenase; AFP, alpha fetoprotein; APTES, (3-aminopropyl)-triethoxysilane; AuNP, Gold colloid; BE, bulk electrolysis; BPO, benzoyl peroxide; bpy, 2,2′-bipyridine; BSA, bovine serum albumin; CL, chemiluminescence; CNT, carbon nanotube; DBAE, 2-(dibutylamino)ethanol; DNA, deoxyribonucleic acid; dsDNA, double-stranded DNA; ECL, electrogenerated chemiluminescence; Fc, ferrocene; FITC, fluorescein thiocyanate; GCE, glassy carbon electrode; IL-6, interleukin-6; ITO, indium tin oxide; LBL, layer-by-layer; MCM-41, type of mesoporous silica; MMP, magnetic microparticle; MPTMS, (3-mercaptopropyl)-trimethoxysilane; MWCNT, multi-walled carbon nanotube; NADH, nicotinamide adenine dinucleotide; NP, nanoparticle; PBS, phosphate buffered saline; PCR, polymerase chain reaction; PEG, polyethylene glycol; PEN, project on emerging nanotechnologies; piq, 1-phenyl isoquinoline; PL, photoluminescence; PSA, prostate specific antigen; QD, quantum dot; RNA, ribonucleic acid; RuNP, $Ru(bpy)_3^{2+}$ doped silica nanoparticle; SCE, saturated calomel electrode; SELEX, systematic evolution of ligand by exponential enrichment; ssDNA, single-stranded DNA; SWCNT, single-walled carbon nanotube; TBrPA, tri(4-bromophenyl)amine; TEA, triethylamine; TEOS, tetraethyl orthosilicate; TMPDA, N^1,N^1,N^3,N^3-tetramethylpropane-1,3-diamine; TPhA, triphenylamine; TPrA, N,N,N-tripropylamine; T–T, thymidine–thymidine; w/o, water in oil; ΔG_{el}, variation of the Gibbs energy due to the electrostatic interactions between the partners of annihilation reaction, when these species are both charged; ΔG_{ES}, variation of the Gibbs energy due to generation of the excited state of a chemical species.

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ECL emission is initiated and controlled by the electrode potential and immobilization of the ECL probes on the electrode surface allows one to reduce the consumption of expensive reagents, simplifies the experimental design, and creates regenerable sensing devices. The organization of the electrode surface is thus the key point to optimize the device performance. Nanoparticles have proved their potential as tools to organize the ECL probes, to increase the active area and to improve the electrochemical properties of the interface. There is an extended research devoted on one hand to optimize the materials, and on the other hand to explore the wide horizon of possibilities that arise from the combination of nanoparticles and ECL probes, co-reagents, (bio)markers and other functional moieties. The results discussed in this review clearly show that the use of nanoparticles aimed to obtain signal enhancement represents one of the most interesting research lines for the development of the ECL technique. The activity in this field is so dynamic that outstanding results could reasonably be expected in the near future.

1. Introduction

The field of *nanotechnology* is constantly broadening its borders and its complexity and, in line with this, the term has evolved over the years. The original meaning is now more properly labelled *molecular nanotechnology*, or *nanoscale engineering* and indicates the research and technology developments involved in designing and using systems and devices in the length scale range of approximately 1–100 nm, objects that are characterized by novel properties rising from their size. As already theorized many years ago [1–3], the properties of bulk materials change very much when very small (even a few atoms) aggregates are taken into account. Metal and semiconductor bulk properties can be explained referring to electrons that occupy energy bands, whereas in single atoms electrons are distributed in discrete energy levels. When only a few atoms are linked together forming very small clusters with dimensions in the range of a few nanometers, their electronic configuration lies somewhat in between the above two limiting cases, it dramatically depends on the cluster size and it can be fully described only by quantum mechanics. The electronic (optical, electrochemical, magnetic, and catalytic) properties of nanoparticles, therefore, differ from those of bulk materials since their valence electrons experience different energies and distributions. A direct consequence is that the properties of these small clusters depend not only upon the components but also dramatically upon their size and shape, along with the environmental conditions that their surfaces experience. This allows for unprecedented control in the field of materials and, by taking advantage of quantum-level properties, devices and systems can be engineered to present exact features and characteristics.

The merging with molecular nanotechnology represents the most advanced frontier of research in many areas such as biology, chemistry, physics, engineering, and computer science. Nanotechnology, in fact, is certainly still a science in its infancy, but it is already affecting our everyday life with many different products, and its further application could potentially bring about great improvements in the life standards of people, with numerous important economic and social implications. All this can explain the continuously increasing interest, efforts and financing devoted to this field. In particular, achievements in the health framework continue to dominate in number and impact. Inexpensive, hand held diagnostic or monitoring kits and slow drug delivering systems, for example, will represent brilliant solutions where adequate medical structures and equipments are not possible or present, and storage capabilities are reduced if not altogether absent.

In this context nanoparticles clearly play a major role. They are usually described as small spheres with controlled dimensions and a radius in the nanometer scale, but their shape can vary very much. The impressive range of interests and applications of nanoparticles arises from their incredible versatility and tunability. A great number of substances can be used, for example, to prepare them, such as carbon (fullerenes, carbon-dots), metals (silver, gold, copper, platinum), metal oxides (zinc, iron, titanium, copper oxides), semiconductors (cadmium selenide, zinc sulphide, etc.), silica, polymers, and many different mixing of two or more of these materials. Moreover, it is possible to derivatize their surface with different capping agents, to easily tune and change their properties such as solubility or affinity, and to introduce the needed functionalities (receptors, reactive sites, electroactive or photoactive moieties, DNA strains, etc.).

In the framework of medical diagnostics, electrogenerated chemiluminescence (ECL, chemiluminescence produced by electrogenerated species in solution) [4,5] is known to offer better performance than other analytical techniques in many applications [4–7]. For the reasons discussed above, the use of nanoparticles aimed to obtain signal enhancement, represents perhaps the most interesting research line for the development of the ECL technique. Although still largely unexplored this approach is, in our opinion, bound to take about the greatest improvements and progresses in the near future. This review aims to give an overview on the state of the art in the precise context of metal complexes-based ECL dyes directly adsorbed on, included in or interacting with nanoparticles of various nature. We have collected some of the most original and inspiring papers of the area published in the last 5 years, and trying to match the main interests of the readers of this journal on coordination chemistry, we have focused only on electrochemically active metal complex systems, and we have quickly realized that this still means, in the majority of cases, structures based on $Ru(bpy)_3^{2+}$ derivatives. We are, however, well aware of the numerous very interesting results obtained with different families of ECL dyes not based on metal complexes, such as above all luminol and quantum dots, and we invite the interested readers to refer to other recent reviews [4–13] for a deeper discussion on them. It has to be noted, moreover, that even if ECL from organic compounds, e.g., polycyclic aromatic hydrocarbons, is typically a very efficient process, the combined use of NPs and organic dyes has been described, at present, in a limited number of papers. In this framework, we have very recently demonstrated the efficient ECL emission from NPs doped with rhodamine and cyanine derivates exploiting an electrochemically induced energy transfer mechanism [14].

It comes out very clearly, also from such a brief introduction, that the scenario of nanoparticles-based ECL is extremely complex due to the very high number of involved variables such as, only to mention a few, the ECL active species, nanoparticles dimensions, materials, shape, capping agents, different interaction/binding among nanoparticles–ECL probes and, in case, with the electrode. For this reason passing from conventional molecular ECL active species to nanoparticles it becomes almost impossible the direct comparison of the performance of different systems, even when the same electrochemical active species is used. This would become possible only exploring the differences on each system incrementally varying each single variable in a systematic way. When comparing results obtained by different research groups worldwide this becomes very difficult since a difference in