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Review

Metal-enhanced luminescence: Current trend and future perspectives- A review

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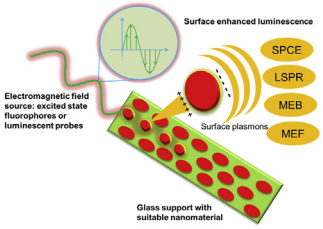
HIGHLIGHTS

- Nanomaterials significantly differ from their bulk counterparts.
- Strong and pronounced photophysical effects at the metal surface provide opportunities for designing novel biosensors.
- Metal-enhanced luminescence increases the quantum yield of luminescent reactions.
- Under optimal conditions, plasmon coupling enhances the optical effects at the nanometal surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Optically enhanced biosensing strategies are prerequisites for developing miniature and highly sensitive multiplexed analytical platforms. Such smart biosensing systems are highly promising for use in the fields of biomedicine and environmental monitoring. Optical signal enhancement during bioassays is attributed to the complex opto-electronic interactions of incoming photonic signals at the nanomaterial interface. Research on the use of metals other than gold and silver for such purposes tends to extend the spectral window to observe luminescence enhancement effects. Such manifold increase in luminescence may be explained by the principles of plasmon coupling, directional emission led high collection efficiency, Rayleigh scattering and related opto-electronic events. The present review begins with a mechanistic description of important phenomena associated with metal-induced luminescence enhancement, particularly focusing on the origin of metal-enhanced luminescence. This review further analyses the hybrid nanostructure capabilities responsible for maintaining unique opto-electronic properties during bio-functionalisation. Current research trends in this area, future scope of this field for designing useful bioassays and concluding remarks are then discussed.

Abbreviations: (BRET), bioluminescence resonance energy transfer; (FRET), fluorescence resonance energy transfer; (AuNPs), gold nanoparticles; (IgG), human immunoglobulin G; (LSPR), localised surface plasmon resonance; (MEB), metal-enhanced bioluminescence; (MEF), metal-enhanced fluorescence; (PRET), plasmon resonance energy transfer; (QDs), quantum dots; (SIFs), silver island films; (AgNPs), silver nanoparticles; (SPs), surface plasmons; (SPCC), surface plasmon coupled chemiluminescence; (SPCL), surface plasmon coupled luminescence; (SPCE), surface plasmon coupled emission; (SPPs), surface plasmon polaritons; (SPR), surface plasmon resonance.

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1. Introduction

In recent years, considerable progress has been witnessed in the production of fabricated, luminescence-based miniature and sensitive optical analytical platforms for their possible applications in the fields of food hygiene, biomedicine and environmental monitoring [1–3]. Designing of such smart biosensing systems requires very high sensitivity. Surface plasmons (SPs) on the surface of metallic nanoparticles have greatly contributed in improving luminescence- and fluorescence-based enhanced biosensing of many different analytes. The emergence of surface plasmon resonance (SPR) peaks in localised nanomaterial regions can simultaneously initiate closely related photo-physical events. The refractive index (RI) of the surrounding medium plays an important role in modulating the SPR wavelength peak. Moreover, even a slight change in RI causes the peak to shift, which forms the basis for designing SPR biosensors. Thus, high RI sensitivities of metallic nanoparticles are prerequisites for designing superior biosensing tools, which depend on shape and size of the nanomaterials tools. Elongated and tapered gold nanoparticles (AuNPs) exhibit higher sensitivity indices than spherical AuNPs [4]. Mathematically, the Drude model for metal electronic structures can be used to explain RI sensitivity. Considering the plasmon frequencies in visible or infra-red regions, the simplified equation of the Drude model can be represented as

$$\lambda_{max} = \lambda_p \cdot \left(2{n_m}^2 + 1\right)^{1/2} \quad (1)$$

in which λ_{max} is the peak wavelength for localised surface plasmon resonance (LSPR), whereas λ_p is the wavelength corresponding to the bulk metal's plasmon frequency, and n_m^2 is the RI. The LSPR shift is approximately linear with small changes in RI [5]. A surge in recent research concerning the role of nanomaterials in constructing smart optical biosensing devices has been observed [6–9]. Metal-enhanced optical phenomena such as metal-enhanced fluorescence (MEF), metal-enhanced bioluminescence (MEB), surface plasmon coupled chemiluminescence (SPCC), plasmon resonance energy transfer (PRET), LSPR and other plasmon-related effects may offer economically feasible solutions to minimize biosensing platforms (Fig. 1) [10]. Table 1 presents the optical enhancement effects, principles and the extensive applications of nanomaterials.

Recently, gold (Au)- and silver (Ag)-based thin nanofilms have been used for observing optically enhanced diagnostic applications [26,27]. One of these optical effects, surface plasmon coupled emission (SPCE), extensively uses these metals because of their ability to maintain unique opto-electronic properties during biofunctionalisation. However, more economic solutions for observing SPCE-based biodiagnostics were investigated using other metals such as zinc (Zn), aluminium (Al) and copper (Cu) [28–36]. SPCE investigations using such alternatives broadened the spectral range, thereby extending the scope of biosensing strategies.

Metallic nanomaterials in close vicinity (<10–200 nm) of luminescence-emitting excited state intermediates such as the keto-1 form of oxyluciferin and C4a-hydroperoxyflavin intermediate may allow the induction of mirror dipoles at the nanometallic surfaces, which leads to strong resonating signals via coupling of plasmonic waves [37–40]. These signals considerably enhance luminescence. In nano-optic and medical diagnostic research, Au nanocolloid is one of the most widely used nanomaterials owing to its easy and stable synthesis, non-toxic nature, size tunability and very high molar extinction coefficient [41–44]. In contrast to using a single metal, alternate approaches involving the amalgamation of two or more metals and nanostructures such as graphene were investigated to explore their optical enhancement effects [45–47]. Use of impregnated Ag in a thin film of zinc oxide (ZnO) coating over a silica substrate was considered as an example of resonant coupling between Ag SPs and ZnO spontaneous emission [48]. In a similar approach, thermally annealed silver island films (SIFs) for MEF have been previously described [49]. Protein-labelled fluorescent compounds were used to coat SIFs for observing distance and size-dependent fluorescence enhancement. Results indicated SP coupling with fluorophore's fluorescence emission. Photon absorption by plasmonic nanomaterials via incident electromagnetic radiation can result in either light scattering or heat dissipation with concomitant luminescence emission. These dual independent events can be analysed by calculating the scattering and absorption cross sections, which are defined as the effective area over which nanoparticles scatter or absorb light [50]. SIF extinction spectra (C_E) comprising both scattering (C_s) and absorption (C_A) components were experimentally proven to be proportional to the sixth power of the Ag ion radius (r) and its cube, respectively, indicating an increase in the scattering contribution when the size of the nanostructure or colloid was increased. Mathematically,

$$C_E = C_s + C_A = \left({k_1}^4 / 6\pi\right) \cdot |\alpha|^2 + k_1 \cdot \mathrm{Im}(\alpha) \quad (2)$$

where k_1 is the wave vector ($2\pi n_1/\lambda_0$), λ_0 is the incident light in medium I_m of RI n_1, and the $|\alpha|^2$ term represents the square modulus of α which is the polarizability of the sphere with radius r as explained in equation (3):

$$\alpha = 4\pi r^3(\varepsilon_m - \varepsilon_1)/(\varepsilon_m + 2\varepsilon_1) \quad (3)$$

where ε_m represents the complex dielectric constant of metal, whereas ε_1 is the dielectric metal constant.

MEF has been investigated in detail and applied in phosphorescent and fluorescent signal enhancement for designing light-