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Chemiluminescence enhancement in the course of luminol oxidation in the presence of metal ions and plasmonic nanoparticles

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The results on chemiluminescence in the presence of plasmonic silver nanoparticles and chemical catalysts: copper, iron, cobalt, and manganese ions are presented. Enhancement of chemiluminescence by both nanoparticles and ions, separately and in combination with silver nanoparticles, is demonstrated. Concentrations of ions and nanoparticles providing maximum enhancement of the chemiluminescent signal were selected. The chemiluminescence enhancement by joint action of nanoparticles and ions exceeds that with silver nanoparticles or ions applied separately. The differences in physical and chemical enhancement mechanisms characteristic of them are clearly demonstrated by comparison of enhanced chemiluminescence spectra.

Keywords: plasmon-enhanced chemiluminescence, Purcell effect, catalysis, silver nanoparticles, free radicals.

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Introduction

Numerous studies have been devoted to chemiluminescence since the first half of the last century. This topic remains relevant to this day. According to World Health Organization (WHO) statistics, the incidence of autoimmune and oncological diseases continues to rise [1]. The primary cause of pathogenesis in several diseases and pathological processes in the human body is oxidative stress. Oxidative stress in the body most commonly arises from high concentrations of free radicals, including reactive oxygen species (ROS) [2]. Sensitive methods for their detection are essential for timely diagnosis.

The low limit of detection characteristic of chemiluminescent methods has led to their widespread use in medicine, particularly for diagnosing autoimmune diseases [3]. Chemiluminescent sensors are also employed in forensics, gas analyzers [4], and pesticide detection systems in agriculture [5].

The broader application of chemiluminescence is, however, limited by its low intensity, which stems from competition between radiative and non-radiative relaxation pathways for electronic excitation energy.

A promising method for enhancing the chemiluminescent signal without directly interfering with the chemiluminescent reaction is to accelerate the radiative transition. This can be achieved when the chemiluminophore molecule is in close proximity to a metal nanoparticle whose plasmon resonance band overlaps with the chemiluminescence band [6–11]. Such an increase in the rate of radiative transitions in an inhomogeneous medium is known as the Purcell effect.

Enhancement of the chemiluminescent signal can also be achieved using chemical catalyst metal ions that accelerate the reaction itself [12]. The interaction of the analyte with metal ions produces a product with higher oxidative activity toward the chemiluminophore molecules, resulting in a faster chemiluminescent reaction and greater emission intensity.

Accordingly, the objective of this study was to identify optimal catalysts among iron, copper, cobalt, and manganese ions, and to determine the concentrations and degree of chemiluminescence enhancement during luminol oxidation by sodium hypochlorite in the presence of plasmonic nanoparticles. In nature, sodium hypochlorite is produced in a reaction catalyzed by the enzyme myeloperoxidase. This process occurs when blood granulocytes contact foreign cells, such as bacteria. Activation of cell surface receptors triggers processes leading to the formation of superoxide radicals [13].

Thus, this study lays the foundation for using chemiluminescence to detect diseases associated with oxidative stress and for developing sensor systems.

Materials and methods

Aqueous solutions of luminol at a concentration of $3.5 \cdot 10^{-4}$ M, sodium hypochlorite ($400\,\mu$M), and NaOH at pH=7 were used in this work.

Spherical silver nanoparticles with a citrate shell (Ag NP) were synthesized via colloidal synthesis using the following procedure [14]:

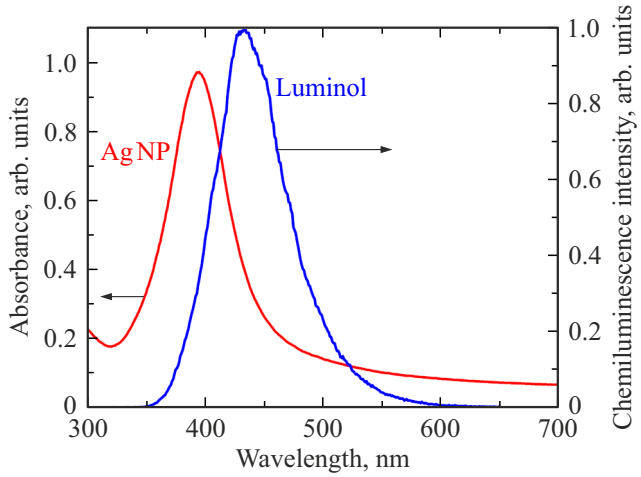

Figure 1. Chemiluminescence spectra during luminol oxidation by sodium hypochlorite (blue curve) and extinction spectrum of citrate-shell silver nanoparticles (red curve).

1) Aqueous solutions of trisodium citrate and $AgNO_3$ at 0.01 M concentration were mixed in a 1:1 volume ratio;

2) Sodium tetrahydroborate 5−6°C was added to deionized water precooled to $NaBH_4$ to prepare a 0.01 M solution, which was then vigorously stirred after preparation;

3) The sodium tetrahydroborate $NaBH_4$ solution was then added dropwise to the vigorously stirred solution ($AgNO_3$ + trisodium citrate) until a volume ratio of 2 : 1 was achieved between the ($AgNO_3$ + trisodium citrate) solutions and the sodium tetrahydroborate $NaBH_4$. The resulting nanosilver solution was aged for approximately 10 min to allow the reaction components to interact. The final nanosilver solution exhibited a dark yellow color.

For synthesis, silver nitrate$AgNO_3$ (OOO „Bertuz“, Russia, purity $\geq$ 99%), trisodium citrate from AppliChem Panreac ($\geq$ 98%), and sodium tetrahydroborate $NaBH_4$ from Chemical Line ($\geq$ 98%) were used. The average hydrodynamic size of the synthesized silver nanospheres, measured by dynamic light scattering of the nanoparticle colloidal solution and confirmed by matching the measured extinction spectrum with the Mie scattering theory calculation [15], was 12 nm.

The choice of silver nanoparticles for plasmonic enhancement of luminol chemiluminescence was motivated by the good overlap between the plasmon band of silver nanoparticles and the luminol chemiluminescence spectrum (Fig. 1), which enables an increase in the radiative transition rate in the „luminol molecule−silver nanoparticle“ system compared to an isolated luminol molecule.

Solutions of copper Cu^{2+}, iron Fe^{2+}, manganese Mn^{2+}, and cobalt Co^{2+} ions were prepared by dissolving copper (II) sulfate $CuSO_4$ (purity $\geq$ 98%), iron (II) sulfate $FeSO_4$ ($\leq$ 99%), manganese (II) sulfate $MnSO_4$ ($\leq$ 98%), and cobalt (II) nitrate CoNO3 ($\leq$ 98%) in deionized water. The reagents were purchased from „Lenreactiv“ (Russia).

Absorption spectra of silver nanoparticle colloidal solutions were measured using an SF-56 spectrophotometer (LOMO, Russia). The chemiluminescence spectrum was recorded using an RF9301 spectrofluorimeter (Shimadzu, Japan) with the excitation source turned off. Hydrodynamic sizes of silver nanoparticles were determined using a Zetasizer Nano analyzer (Malvern Panalytical, UK). Chemiluminescence intensity was measured with an H11890 photon counter (Hamamatsu, Japan).

Chemiluminescence was recorded as follows: a mixture of aqueous luminol solutions (100 μl, $3.5 \cdot 10^{-4}$ M), metal ions (25 μl, $10^{-8}-10^{-4}$ M) and silver nanoparticles (25 μl, 0−10 μM) was supplemented with 400 μM sodium hypochlorite solution serving as the analyte, while maintaining neutral acidity (pH = 7) by adding sodium hydroxide. Upon mixing the analyte with the chemiluminophore, blue emission (chemiluminescence) was observed, and its intensity was measured as a function of time using the photon counter; after the reaction ceased and emission stopped, analyte was added again, and measurement was repeated. The enhancement factor, defined as the ratio of chemiluminescence intensity in the presence of catalysts or plasmonic nanoparticles to that in their absence, was evaluated using the peak signal value averaged over four consecutive measurements.

Results and discussion

In the presence of metal ions, the intensity of luminol chemiluminescence during oxidation by sodium hypochlorite increased. This enhancement depended on both the specific metal and the ion concentration in solution. Figure 2 shows the measured dependencies of the chemiluminescence enhancement factor on metal ion concentrations.

With increasing iron ion concentration up to 10^{-7} M luminol chemiluminescence reaches 3.5-fold enhancement.

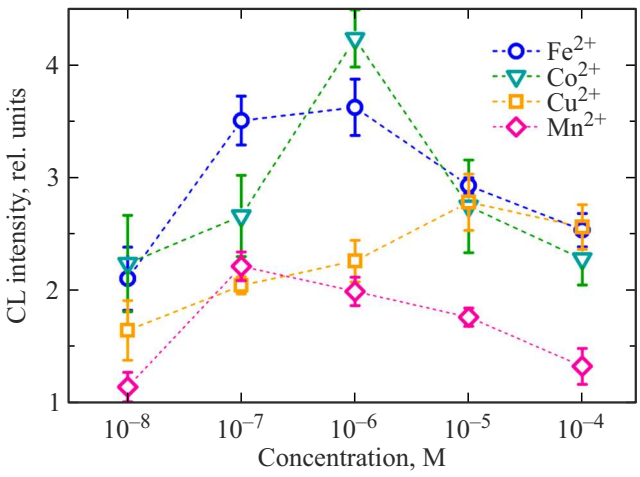

Figure 2. Dependence of the luminol chemiluminescence enhancement factor during oxidation by hypochlorite (400 μM) on the concentrations of iron Fe^{2+}, cobalt Co^{2+}, copper Cu^{2+}, and manganese Mn^{2+} ions in solutions at pH = 7.

Enhancement of chemiluminescence during luminol oxidation by hypochlorite (400 μM) in solution at pH=7 with metal ions at optimal concentrations, with 10^{-5} M silver nanoparticles and without nanoparticles

Ion	Concentration, M	Without Ag,NP	With Ag NP
iron Fe^{2+}	10^{-6}	3.5 ± 0.4	4.7 ± 0.4
copper Cu^{2+}	10^{-5}	2.7 ± 0.2	3.5 ± 0.3
cobalt Co^{2+}	10^{-6}	4.0 ± 0.2	7.3 ± 0.4
manganese Mn^{2+}	10^{-7}	2.1 ± 0.1	3.2 ± 0.3

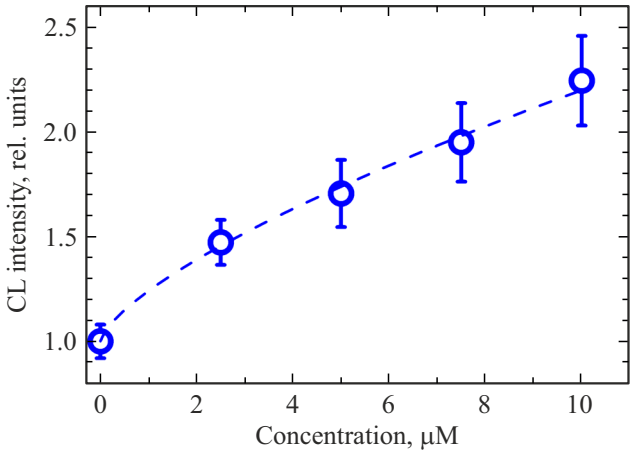

Figure 3. Dependence of the luminol chemiluminescence enhancement factor during oxidation by hypochlorite (400 μM) on the concentration of silver nanoparticles (Ag,NP) in solution at pH = 7.

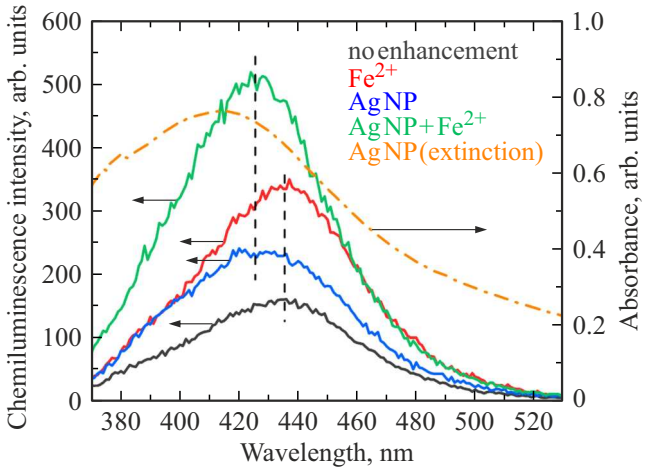

Figure 4. Chemiluminescence spectra during luminol oxidation by sodium hypochlorite without additives, in the presence of silver nanoparticles Ag,NP, iron ions Fe^{2+} and combined Ag,NP and Fe^{2+}. Vertical dashed lines indicate the positions of luminescence maxima without nanoparticles (435 nm) and with nanoparticles (425 nm).

Beyond a catalyst concentration of 10^{-6} M the chemiluminescence intensity decreases. This is attributed to the reaction product of iron ions and hypochlorite interacting not only with luminol molecules but also with iron ions themselves [16]. A similar pattern is observed for chemiluminescence in the presence of other metal ions.

Cobalt ions provide the highest chemiluminescence enhancement (4-fold at 10^{-6} M) concentration), followed by iron ions (3.5-fold at 10^{-7}–10^{-6} M), copper ions (2.7-fold at 10^{-5} M) and manganese ions (2-fold at 10^{-5} M), consistent with published data on catalysis in chemiluminescence enhancement [12].

Chemiluminescence intensity also depends on silver nanoparticle concentration; dilution of the synthesized solution reduces it (Fig. 3).

Thus, an optimal concentration of 10^{-5} M of the original citrate-shell silver nanoparticle solution was selected, which provided 2–2.5-fold enhancement of luminol chemiluminescence. At higher concentrations, chemiluminescence quenching may occur due to non-radiative energy transfer via the FRET mechanism [17].

The enhancement factors for chemiluminescence in the presence of metal ions at optimal concentrations with silver nanoparticles or ions alone are presented in the table above.

In all cases, the presence of both catalyst (metal ions) and silver nanoparticles results in greater luminol chemiluminescence enhancement than using either catalyst or plasmonic nanoparticles alone. Among the ion catalysts, cobalt ions yield the highest enhancement: fourfold without silver nanoparticles and sevenfold with them. Iron, copper, and manganese ions follow in descending order of enhancement factor.

Whereas metal ions merely accelerate the oxidation reaction, thereby enhancing the associated chemiluminescence without altering its spectrum, silver nanoparticles not only increase the intensity but also shift the spectrum, as illustrated in Fig. 4 for iron ion catalysis.

The Purcell effect with plasmonic nanoparticles enhances chemiluminescence only in the spectral region overlapping the silver nanoparticle absorption and luminol chemiluminescence spectra. Since the silver nanoparticle absorption spectrum lies at shorter wavelengths relative to the luminol chemiluminescence spectrum, the near-field effect of the nanoparticles induces a hypsochromic shift in the chemiluminescence spectrum [18].

The spectral differences in chemiluminescence with and without silver nanoparticles illustrate the distinct enhance-

ment mechanisms — chemical catalysis by metal ions and the „nanoantenna“ effect (Purcell) by plasmonic nanoparticles.

Conclusion

This study demonstrates enhancement of chemiluminescence during luminol oxidation by hypochlorite in biologically neutral media (pH=7) using metal ions and plasmonic silver nanoparticles via distinct mechanisms; concentrations of nanoparticles and ions providing maximum enhancement factors were determined.

Comparison of chemiluminescence spectra during luminol oxidation by sodium hypochlorite in the presence of silver nanoparticles and iron ions separately and jointly illustrates the difference between physical and chemical enhancement mechanisms, demonstrated here for the first time.

Optimal concentrations of plasmonic nanoparticles and metal ions for enhancing luminol chemiluminescence in biologically neutral media (pH=7) during oxidation by sodium hypochlorite were determined. The best — sevenfold — enhancement is achieved with the combination of cobalt ions and silver nanoparticles. Such enhancement is substantial enough for applications in real chemiluminescent sensor systems for detecting elevated oxidant levels.

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Conflict of interest

The authors declare that they have no conflict of interest.

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