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Shining Light on Nanochemistry Using Silver Nanoparticle-Enhanced Luminol Chemiluminescence

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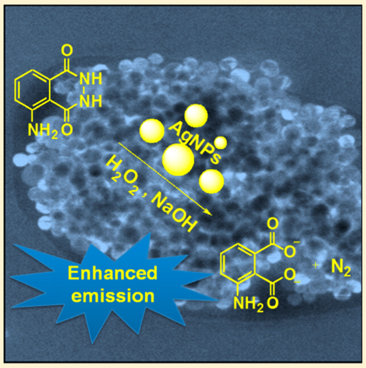
ABSTRACT: A combination of the well-known luminol chemiluminescence with noble metal nanochemistry provides an easy, original, and appealing way to introduce nanotechnology topics via a classroom demonstration. Citrate-stabilized silver nanoparticles are used to enhance the emission of light from the luminol–hydrogen peroxide system. A proposed reaction mechanism, based on the effect of different reactive oxygen species scavengers on the course of the reaction, is described.



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Chemiluminescence, the emission of light resulting from chemical reactions, has a peculiar fascinating appeal and has been recognized as the most “exocharmic” kind of reaction.[1] The oxidation of 3-aminophthalhydrazide, best known as luminol, is a popular chemiluminescent reaction, and its protagonist role in demonstrations, lectures, and chemistry shows is attested to by the number of articles that have been published since the report of Huntress et al.[2] Many improvements have been suggested, ranging from the use of different reactant mixing strategies[3−7] to the addition of oscillating systems[8] and clock reactions.[9] The emission of light from luminol occurs through an oxidation process requiring air, hydrogen peroxide, or bleach,[10,11] typically in the presence of a metal catalyst, such as the iron contained in blood.[12,13] The emission of light can also be obtained electrochemically.[14,15] The chemiluminescence of luminol displays a bright blue color, which can be modified by the addition of fluorophores.[16] This reaction has widespread practical applications and has been reported as an effective way to introduce forensic[17] and analytical[18] techniques. In the present article, an unusual way to introduce students to nanochemistry using luminol chemiluminescence is proposed.

The increasing relevance of nanotechnology and nanochemistry in chemical education has been pointed out recently.[19,20] Moving from the bulk to the nanoscale, the physicochemical properties of materials undergo formidable changes, and noble metals are especially suitable to illustrate such variations. Nanoparticles also have relevant application in catalysis; however, only one experiment (using copper nanoparticles) has been reported on this subject in this Journal.[21]

One of the most striking properties of gold and silver nanoparticles is color, which strongly depends on the size, shape, environment, and state of aggregation of the particles. Such a peculiar property is due to a phenomenon known as surface plasmon resonance, a collective periodic motion of electrons excited by electromagnetic waves of appropriate frequency (plasmon resonance frequency).[22] Silver nanoparticles are easy to synthesize from cheaper precursors than gold nanoparticles (typical prices are ~\$3.6/g for $AgNO_3$ and ~\$241/g for $HAuCl_4$),[23] display strong optical properties, and have good chemical stability. For these reasons, they have been the subject of many publications in this Journal regarding their synthesis, characterization,[24−26] and application in surface-enhanced Raman scattering.[27,28] Silver nanoparticles are also protagonist of a popular “stained glass” demonstration.[29,30]

A novel version of the hydrogen peroxide-mediated oxidation of luminol is proposed here in which silver nanoparticles are used to trigger and enhance the chemiluminescence emission. This approach has promising application for the realization of bioassays[31,32] and biosensors.[33] Chemiluminescence methods require simple instrumentation and are characterized by good reproducibility and a wide dynamic range, but they lack selectivity and sensitivity, which can be obtained by using gold and silver nanoparticles. Interestingly, not only the nature of the metal employed but also the shape of the nanoparticles (e.g., nanorods,[34] nanotriangles[35]) seem to have an importance for these reactions.

The aim of this demonstration is to combine the appealing character of chemiluminescent reactions with the catalytic properties displayed by noble metal nanoparticles in a

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synergistic way to stimulate interest in both photochemistry and nanochemistry and to show the relevance and potentialities of the latter.

PREPARATION

Before performing the demonstration, it is necessary to synthesize the silver nanoparticles and to prepare a 10 mM luminol stock solution in 100 mM aqueous NaOH. This solution can be stored at 4 °C for no more than 2 weeks. Once the stock solutions and the silver particles have been prepared, this demonstration requires less than 1 h to be performed. It is best to simultaneously carry out the experiment with and without the silver nanoparticles to allow direct comparison of the results.

Chemicals

Silver nitrate, trisodium citrate dihydrate, sodium borohydride, sodium hydroxide, 3-aminophthalhydrazide (luminol), 30 wt % hydrogen peroxide, sodium ascorbate, sodium 4,5-dihydroxybenzene-1,3-disulfonate (tiron), superoxide dismutase (SOD), *tert*-butyl alcohol, dimethylsulfoxide, and sodium azide were purchased from Aldrich and used as received. Milli-Q water (resistivity ~18 MΩ cm^{-1}, Barnstead) was always used.

Synthesis of Citrate-Stabilized Silver Nanoparticles

A solution of 0.15 g of silver nitrate in 25 mL of water was added under stirring to a solution of 0.5 g of trisodium citrate in 125 mL of water. The clear, colorless solution was poured in a three-necked, round-bottomed, 250 mL flask (equipped with a mechanical stirrer and an addition funnel) and cooled in an ice bath. An ice-cooled solution of sodium borohydride (0.0125 g, dissolved in 30 mL of water) was then added through the funnel dropwise under stirring (~400 rpm). The resulting dark-brown suspension was left under stirring for additional 5 min and aged before use for 24 h at 4 °C and stored at this temperature. The dark color is due to the relatively high concentration of nanoparticles and changes to a bright yellow upon dilution with water. The mean particle diameter, measured by electron microscopy, was ~10 nm. The concentration of silver nanoparticles, assuming that all the precursor had been reduced to zerovalent metal, was 5 mM.

DEMONSTRATION

In a flask, 1.5 mL of the 10 mM luminol solution was diluted to 50 mL with water, and 300 μL of silver nanoparticle suspension was added to obtain a bright yellow mixture. The same solution was prepared without adding the nanoparticle suspension. The room was darkened, and 510 μL of 30 wt % hydrogen peroxide was added to both mixtures. Immediately after the hydrogen peroxide addition to the solution with the nanoparticles, a blue emission started, lasting for about 10 min. The emission of light was accompanied by the dissolution of silver nanoparticles because the yellow color characteristic of silver nanoparticles disappeared, leaving a colorless solution (Figure 1). No emission of light could be observed in the solution without the nanoparticles.

HAZARDS

Silver nitrate is toxic and an irritant; its contact with skin leads to temporary, dark-colored stains. Sodium borohydride is an irritant and flammable; it generates hydrogen gas by reacting with water. Luminol is an irritant and toxic. Sodium hydroxide is corrosive. Concentrated (30 wt %) hydrogen peroxide is toxic and corrosive, causes severe skin burns and eye damage, is harmful if swallowed, and may be harmful if inhaled. It is a strong oxidizer, which may cause fire or explosion. Tiron and *tert*-butyl alcohol are irritants. Dimethylsulfoxide is an irritant and permeator. Sodium azide is fatal if swallowed or in contact with skin, it is explosive and may react with lead and copper plumbing to form highly explosive metal azides. Sodium azide should not be manipulated by students. Protective gloves and goggles are mandatory.

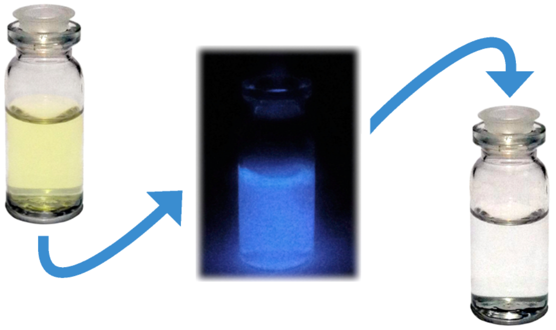


Figure 1. From left to right: the reaction mixture before the addition of hydrogen peroxide; the emission of light; and dissolution of the silver particles, resulting in a colorless solution.

DISCUSSION OF THE MECHANISM

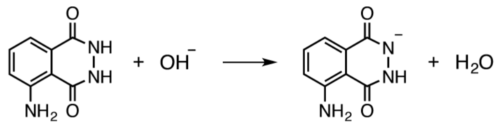
Background

The mechanism leading to luminol chemiluminescence in aqueous solution has been thoroughly investigated in the literature. The classical mechanism describes the ionization of the luminol molecule; then its oxidation, yielding an excited singlet state of 3-aminophthalate anion; and eventually, the emission of a photon by this species, generating a bright blue light.[36,37] For the luminol—hydrogen peroxide system, reactive oxygen species such as the superoxide radical anion and hydroxyl radical have been identified[38,39] as relevant intermediates. Without a catalyst, the oxidation of luminol mediated by hydrogen peroxide in an alkaline medium is relatively slow, thus leading to a weak emission of light.

Silver Nanoparticle—Enhanced Luminol Chemiluminescence

The enhancing effect of silver nanoparticles on the luminol—hydrogen peroxide chemiluminescent system is demonstrated because no emission of light could be observed in their absence.

The question is: Why do silver nanoparticles dramatically enhance the emission of light? A direct interaction is possible between surface plasmons and the light emitted from a chemiluminescent reaction[40] resulting in an increase of the quantum efficiency of emission, but in the case discussed here, the emission enhancement is more probably due to catalytic surface effects and could be ascribed to an interaction of silver nanoparticles with the reactants and with the intermediates (eqs 1—4). Silver nanoparticles can catalyze the decomposition of hydrogen peroxide into reactive species such as the hydroxyl radical and superoxide anion, which in turn react with luminol to give the light emission.[41]



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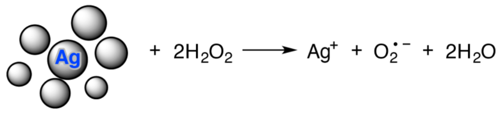

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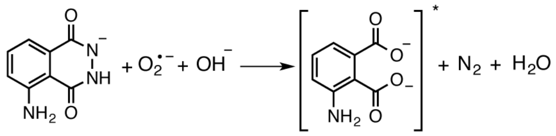

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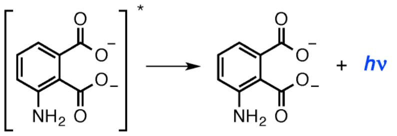

(4)

According to eq 2, superoxide ion can be generated by the direct oxidation of silver particles,[42,43] but this is in contrast to the observation that silver dissolution did not occur when silver nanoparticles were mixed with alkaline hydrogen peroxide. Nanoparticles dissolved only in the presence of luminol. It is known that oxidative etching of metal nanoparticles can be accelerated by nucleophilic reagents and electron acceptors. Adsorption of nucleophiles on the particle surface modifies both the surface charge density and the Fermi level, producing oxidation and aggregation phenomena that are reflected in the absorption spectrum as a red shift and broadening of the plasmon resonance peak (Figure 2).[44] Luminol can act as a nucleophile owing to the amino group, whereas hydrogen peroxide behaves as an electron acceptor. In addition, the 3-aminophthalate anion can act as a complexing agent for Ag^+, contributing to the etching process. It is interesting to note that other oxidants, such as silver nitrate and copper sulfate, in presence of sodium bromide as a nucleophile have been reported to promote the light emission by reacting with luminol in the presence of silver nanoparticles.[32,45]

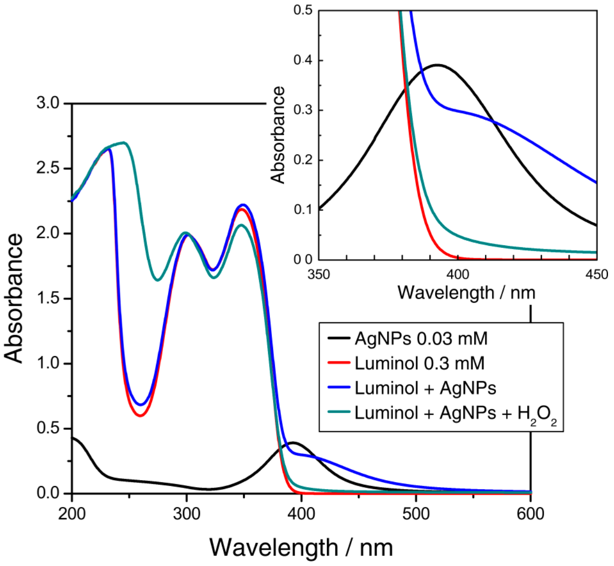

Figure 2. UV−vis spectra of the reactants and of the chemiluminescent system. The inset shows in detail the changes experienced by the silver plasmon resonance band (λ_{max} 393 nm): in the presence of luminol, the absorption maximum red-shifts, and the intensity decreases as a result of peak broadening; after the reaction, the plasmon band disappeared as a result of the particles' dissolution.

Investigation of the Scavengers

The effect of different scavengers has been investigated to evaluate the role of the most relevant reactive oxygen species (ROS), such as the superoxide anion radical, hydroxyl radical, and singlet oxygen in the chemiluminescent reaction. Ascorbate is a well-known free radical scavenger and, as a classical reducing agent, can terminate ROS by electron transfer.[46] Quenching of chemiluminescence was observed in the presence of sodium ascorbate, thus confirming the radical reaction pathway in which the generation of free radicals appears to be the critical controlling factor. Superoxide dismutase (SOD) and tiron were tested to prove the involvement of $O_2^{\bullet -}$. SOD catalyzes the dismutation of superoxide into ground-state molecular oxygen and hydrogen peroxide, whereas tiron is directly oxidized by superoxide to a semiquinone and a peroxide.[47] As in the case of ascorbate, the chemiluminescence of luminol was quenched in the presence of these scavengers. *tert*-Butyl alcohol and dimethylsulfoxide are efficient $^{\bullet}OH$ scavengers, and sodium azide deactivates singlet oxygen,[48] but their addition to the chemiluminescent system did not modify the apparent intensity of emission. These results are summarized in Table 1. As was confirmed by UV−vis spectroscopy, none of the tested scavengers had significant influence on the aggregation state of the nanoparticles.

Table 1. Effect of Different Reactive Oxygen Species Scavengers on the Luminol−H_2O_2−AgNPs System

scavenger	scavenged species	concentration/ mM	effect on chemiluminescence
sodium ascorbate	nonspecific	10	quenching
tiron	superoxide O_2^-	10	quenching
superoxide dismutase (SOD)	superoxide O_2^-	10	quenching
tert-butyl alcohol	hydroxyl radical $^{\bullet}OH$	10	
dimethylsulfoxide	hydroxyl radical $^{\bullet}OH$	10	
sodium azide	singlet oxygen $^1O_2$	10	

Many other scavengers can be tested; for example, thiourea, sodium salicylate, benzoate, and formate have been reported to act as efficient hydroxyl radical scavengers.[49] Studying the effect of hydroxybenzenes would be of great interest, because it has been reported that although dihydroxybenzenes act as quenchers, trihydroxybenzenes such as gallic acid are capable of enhancing luminol chemiluminescence by generating the superoxide anion radical.[50−52] Another interesting test would be to substitute NaOH with Na_2CO_3 because it is known that alkaline carbonates can react with hydrogen peroxide, generating reactive percarbonate species.[46] Considering all the above, a further investigation of this reaction could be the subject of an undergraduate research project.

■ CONCLUSIONS

Silver nanoparticles can efficiently enhance the chemiluminescent reaction of luminol with hydrogen peroxide because of their peculiar redox properties. This demonstration is suited to introduce and illustrate, both at undergraduate and graduate levels, highly relevant topics, such as redox reactions, catalysis, photochemistry, materials chemistry, and nanotechnology. It requires very simple apparatus and reagents, which makes it easily affordable.

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Notes

The author declares no competing financial interest.

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