Chemical Engineering Journal 144 (2008) 483–488

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Sensitized chemiluminescence of luminol catalyzed by colloidal dispersions of nanometer-sized ferric oxides

T.M. Triantis[a], K. Papadopoulos[a,*], E. Yannakopoulou[a], D. Dimotikali[b], J. Hrbáč[c], R. Zbořil[c]

[a] Institute of Physical Chemistry, NCSR 'Demokritos', 15310 Agia Paraskevi, Athens, Greece
[b] Chemical Engineering Department, N.T.U. Athens, 15780 Zografou, Athens, Greece
[c] Department of Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic

ARTICLE INFO

Article history:
Received 1 November 2007
Received in revised form 10 July 2008
Accepted 14 July 2008

Keywords:
Luminol
Chemiluminescence
Ferric oxides
Nanoparticles
Catalysis

ABSTRACT

Colloidal solutions of ferric oxide nanoparticles of different particle size and surface area characteristics enhance the intensity of the chemiluminescent (CL) reaction of luminol with hydrogen peroxide up to 18-fold and accelerate the rate of the reaction time to 86-fold. The sample with the highest enhancement was applied in the determination of hydrogen peroxide and the estimation of hydrogen peroxide scavenging activity of selected antioxidant compounds. Hydrogen peroxide was determined down to 1.25×10^{-3} M (S/N = 3). Regarding the hydrogen peroxide scavenging activities of the selected organic antioxidants, it was found that mono- and dihydroxylated phenols (tyrosol, catechin and caffeic acid) exhibit up to one order of magnitude higher scavenging activity than trihydroxylated phenols (gallic acid and pyrrogallic acid), vitamins E and C, and amino acid cysteine.

1. Introduction

Chemiluminescence (CL) is acknowledged to be one of the most highly sensitive analytical techniques [1–5] with a wide range of applications in diverse fields, such as biotechnology [6], pharmacology [7], food analysis [8], and clinical and environmental assays [9,10]. In most of these techniques, luminol is the chemiluminescent of choice and hydrogen peroxide the oxidation reagent. The sensitivity of these reactions increases dramatically in the presence of metal ions and enzymes [11–14] and as recently mentioned also in the presence of metal nanoparticles [15–17]. In the latter case, the efficiency of light reactions depends strongly on the particle size and surface properties of nanomaterials [18–21]. To the best of our knowledge, with the exception of Zhengping's work [22], nothing is reported about the catalytic activity of ferric oxide nanoparticles in CL reactions. Although it is known that many organic compounds are easily oxidized by hydrogen peroxide in the presence of iron oxides [23–25], these catalysts have not been used yet in CL reactions. Using 8-hydroxyquinoline we could, in a model preparation procedure, produce colloidal solutions of ferric oxide nanoparticles at room temperature and used them in the CL reaction of luminol with hydrogen peroxide. The obtained enhanced and accelerated light signals of this CL reaction were applied for the determination of hydrogen peroxide as well as for the estimation of the hydrogen peroxide scavenging activity of some selected phenolic antioxidants.

2. Experimental

2.1. Equipment

Chemiluminescence measurements were performed on a 1250 Bio-Orbit luminometer with the timer circuitry disconnected. The luminometer (output range 1.0 mV to 10 V) is equipped with a Hamamatsu photomultiplier tube (HAM 105-21) with side window and spectral range from 300 to 620 nm, connected to a potentiometer chart recorder (GOW-MAC Instrument Co., Model 70-150) or personal computer equipped with a homemade software program which allows for the continuous monitoring and analysis of the output signal. Transmission electron microscopy (TEM) studies were undertaken with a FEI CM20 TEM operating at 200 kV. Infrared spectra were recorded on a Nicolet 6700 Fourier transform spectrometer. The content of iron in colloidal solutions was determined by atomic absorption instrument (GBC, Avanta GF 3000) using 25 ppm ferric oxide dispersion as a standard.

2.1.1. Materials

The commercial nanometer-sized iron oxide powders such as α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 (Nos. 1–4) were purchased from Nanotek and Aldrich and used without any additional treatment

* Corresponding author. Tel.: +30 210 6503647; fax: +30 210 6511766.
E-mail address: kyriakos@chem.demokritos.gr (K. Papadopoulos).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.07.035

Table 1
Physical data of various colloidal dispersions of ferric oxide nanoparticles and their effects on the CL intensity and acceleration reaction time of luminol with hydrogen peroxide

No.	Nanomaterial	Commercial products or prepared from	Surface area (m^2/g)	Particle size (nm)	Intensity[a] (mV)	Reaction time[a] (min)
1	α-Fe_2O_3	Nanotek	20	20–40	420	106.6
2	γ-Fe_2O_3	Nanotek	43	5–100	2146	13.8
3	Iron (III) oxide	Aldrich	245	5–25	2122	17.9
4	Iron (II, III) oxide	Aldrich	>60	22–30	1340	37.4
5	Iron (III) oxide	Aldrich	–	<5 μm	770	115.2
6	Amorphous Fe_2O_3	$Fe_4[Fe(CN)_6]3$ (PB)	210	3–4	7766	2.3
7	Amorphous Fe_2O_3	$FeC_2O_4{\cdot}2H_2O$	401	2–3	4943	4.8
8	Mixture of amorphous Fe_2O_3 (63%) and α-Fe_2O_3 (37%)	$FeC_2O_4{\cdot}2H_2O$	288	5–7	3909	6.6
9	Mixture of amorphous Fe_2O_3 (7%) and α-Fe_2O_3 (93%)	$FeC_2O_4{\cdot}2H_2O$	154	10–15	2652	12.7

[a] These values determined at the time where the light signal reached its maximum intensity; the light intensity and reaction time of the blank reaction were 447 mV and 197.6 min, respectively.

Table 2
Analytical characteristics of the corresponding linear regression equations AA_I (%) = $a + bC$ (antioxidant activity vs. concentration) for the estimation of hydrogen peroxide scavenging activity of selected organic antioxidants

No.	Organic compounds	Linear range (M)	a	b	Sy/x	r^2
1	Vitamin E	2.5×10^{-5} to 2.5×10^{-3}	9.58	20,424	3.38	0.981
2	Cysteine	2.5×10^{-5} to 2.5×10^{-3}	10.7	6,622	1.35	0.973
3	Tyrosol	2.5×10^{-5} to 2.5×10^{-4}	9.9	179,213	3.06	0.988
4	Chlorogenic acid	2.5×10^{-4} to 1.87×10^{-3}	−11.1	55,620	3.21	0.995
5	Catechin	2.5×10^{-5} to 2.5×10^{-4}	10.67	236,459	3.27	0.992
6	Pyrrogallic acid	2.5×10^{-5} to 6.25×10^{-4}	11.31	33,895	3.99	0.972
7	Caffeic acid	1.25×10^{-4} to 6.25×10^{-4}	−6.7	141,787	3.32	0.964
8	Ascorbic acid	8.25×10^{-4} to 2.25×10^{-3}	−12.7	25,135	1.16	0.996
9	Gallic acid	2.5×10^{-4} to 2.25×10^{-3}	7.11	13,726	1.04	0.996

(Table 1). For comparison reasons, the micrometer-sized iron (III) oxide was included in the study (No. 5). All other nanomaterials were prepared and characterized in our laboratories according to previously described procedures [26,27]. Amorphous Fe_2O_3 (No. 6, particle size 3–4 nm, surface area 210 m^2/g) was prepared by thermal treatment of powdered Prussian blue (PB, Sigma–Aldrich) in air at 250 °C for 1 h [26]. The sample 7 (amorphous Fe_2O_3, the size range of 2–3 nm, surface area 401 m^2/g), sample 8 (a mixture of amorphous Fe_2O_3 (63%) and α-Fe_2O_3 (37%), the size range of 5–7 nm, surface area of 288 m^2/g) and sample 9 (a mixture of amorphous Fe_2O_3 (7%) and α-Fe_2O_3 (93%), the size range of 10–15 nm, surface area 154 m^2/g) were prepared by controlled thermal treatment of iron (II) oxalate in air at 175 °C for 6, 17 and 100 h, respectively [27]. Crystal structures and phase composition of all synthesized iron oxides were previously confirmed by XRD and ^{57}Fe Mössbauer spectroscopy and published in papers listed as [26,27].

All other chemicals used in this work were of a high purity and purchased from Aldrich except of caffeic acid and catechin, which were obtained from Fluka. The names of all antioxidants used in this work are given in Tables 2 and 3. Ultrapure water was obtained by a Milli-Q PLUS 185 water system (Millipore, Beddord, MA, USA).

2.2. Preparation of colloidal nanomaterial dispersions

The colloidal solutions of ferric oxide nanomaterials were prepared by the following procedure: 5.0 mg solid ferric oxides were added in an aqueous sodium hydroxide solution (50 mL, 0.1 M) containing 50 mg 8-hydroxyquinoline and the resulting mixture sonicated for 30 min (solution A). After leaving the mixture in the dark for 1 h the supernatant solution was collected and used as catalyst working solution for CL measurements. These colloidal catalyst solutions remain stable at least for 5 days as verified by chemiluminescence measurements. Other attempts to bring solid ferric oxide nanomaterials into colloidal solutions using anionic, cationic or neutral surfactants or other organic dispersants such as nitrilotriacetic acid, 2,2-bipyridine and polyethylene glycols failed. 1,10-Phenanthroline was a good colloidal dispersant for ferric oxides, but its effectiveness on the luminol CL reaction with hydrogen peroxide was inferior when compared to 8-hydroxyquinoline.

2.3. Preparation of working solutions

Working colloidal solutions of ferric oxide nanoparticles were prepared as mentioned before (solution A). Alkaline aqueous working solutions of luminol (5.0×10^{-5} M), solution B, were prepared

Table 3
Hydrogen peroxide scavenging activities (IC-50 and TC-50) of some organic compounds estimated from the reduction of chemiluminescence intensity or retardation reaction time of luminol and hydrogen peroxide catalyzed by ferric oxide catalyst No. 6

No.	Organic compounds	Hydrogen peroxide scavenging activity (M)	
		IC-50	TC-50
1	Vitamin E	1.97×10^{-3}	2.94×10^{-3}
2	Cysteine	5.93×10^{-3}	4.21×10^{-3}
3	Tyrosol	2.23×10^{-4}	3.35×10^{-4}
4	Chlorogenic acid	1.09×10^{-3}	1.28×10^{-3}
5	Catechin	1.66×10^{-4}	7.48×10^{-4}
6	Pyrrogallic acid	1.14×10^{-3}	1.51×10^{-3}
7	Caffeic acid	3.99×10^{-4}	5.18×10^{-4}
8	Ascorbic acid	2.46×10^{-3}	1.16×10^{-3}
9	Gallic acid	3.12×10^{-3}	3.24×10^{-3}

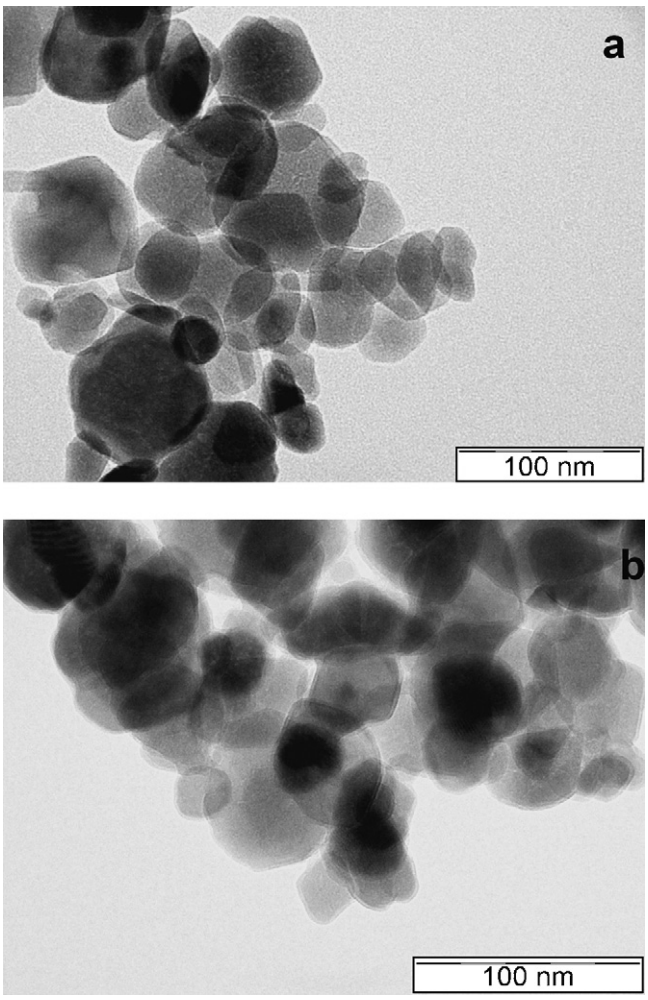


Fig. 1. TEM images of (a) non-coated and (b) coated ferric oxide nanoparticles (No. 1) with 8-hydroxyquinoline.

by consecutive dilutions of a stock solution of luminol (0.01 M) with 0.1 M sodium hydroxide. Working solutions of hydrogen peroxide (0.1 M) were daily fresh prepared by appropriate dilution of commercial 30% (w/v) aqueous hydrogen peroxide with ultrapure water. Working solutions of antioxidant compounds mentioned in Table 3 were prepared by appropriate dilution of their corresponding alkaline stock solutions (0.1 M) with 0.1 M sodium hydroxide solution.

2.3.1. Chemiluminescence measurements

Depending on the purpose of application of catalyzed CL reaction of luminol, the following CL measurements were performed: (a) In order to compare the effectiveness of different ferric oxide nanoparticles on the luminol CL reaction, the light reactions were initiated by adding 200 μL hydrogen peroxide (0.1 M) into a mixture containing 200 μL colloidal catalyst solution A and 200 μL luminol solution B. The light intensities and reaction times obtained compared with those of the corresponding blank reaction, where no catalyst was present (200 μL luminol solution B, 200 μL hydrogen peroxide (0.1 M) and 200 μL sodium hydroxide aqueous solution (0.1 M) containing 0.1% (w/v) 8-hydroxyquinoline). Hydrogen peroxide was added into the reactor cell by a Hamilton syringe through a septum. All measurements were repeated five times at room temperature. (b) For the quantification of hydrogen peroxide, the light reactions were initiated by adding 200 μL hydrogen peroxide solutions of various concentrations into a mixture containing 200 μL alkaline luminol solution B and 200 μL colloidal solution A of catalyst No. 6. This catalyst was chosen due to its highest effect on the CL intensity and acceleration reaction time of light signals (Table 1). (c) For the estimation of antioxidant activities, the light reactions were initiated by adding 200 μL hydrogen peroxide of 0.1 M to a mixture containing 200 μL alkaline luminol solution B, 200 μL colloidal solution A of catalyst No. 6 and 200 μL alkaline aqueous solution of antioxidants of various concentrations (1.0×10^{-5} to 1.0×10^{-2} M).

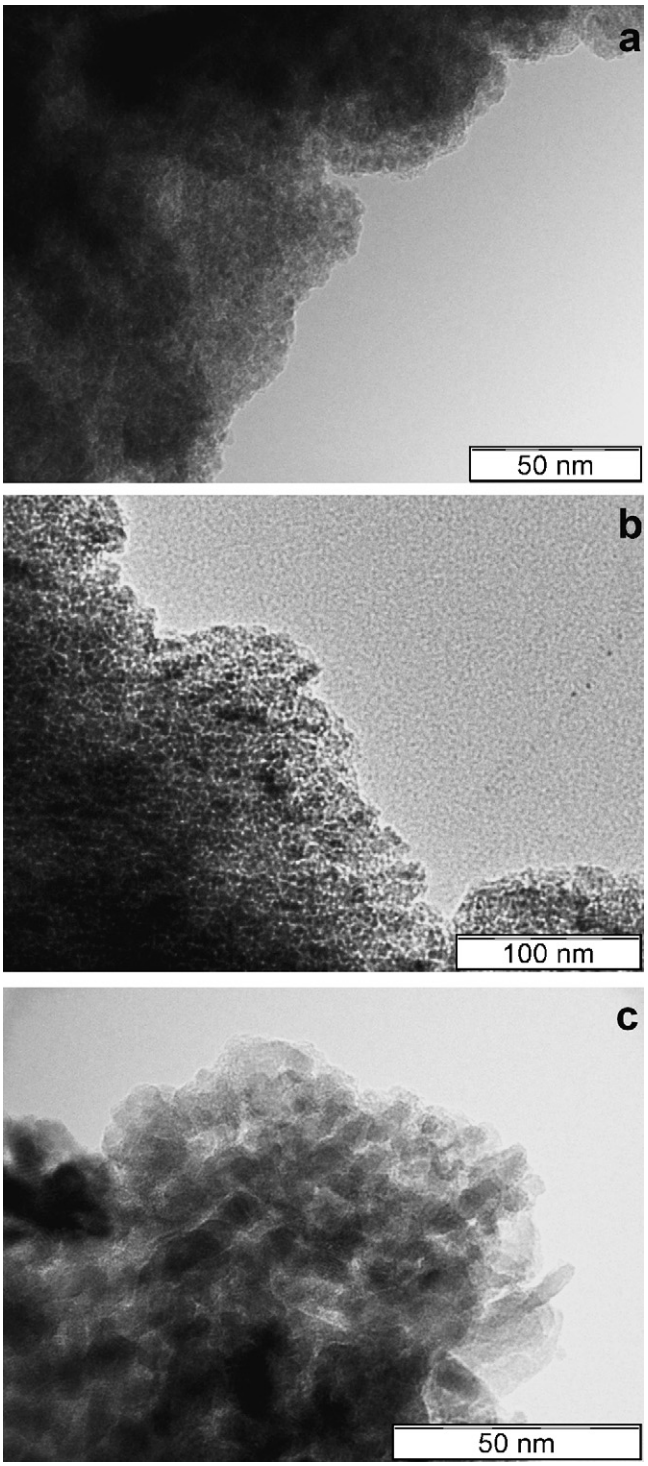


Fig. 2. TEM images of ferric oxide nanoparticles No. 6 (a), No. 7 (b) and No. 9 (c) coated with 8-hydroxyquinoline.

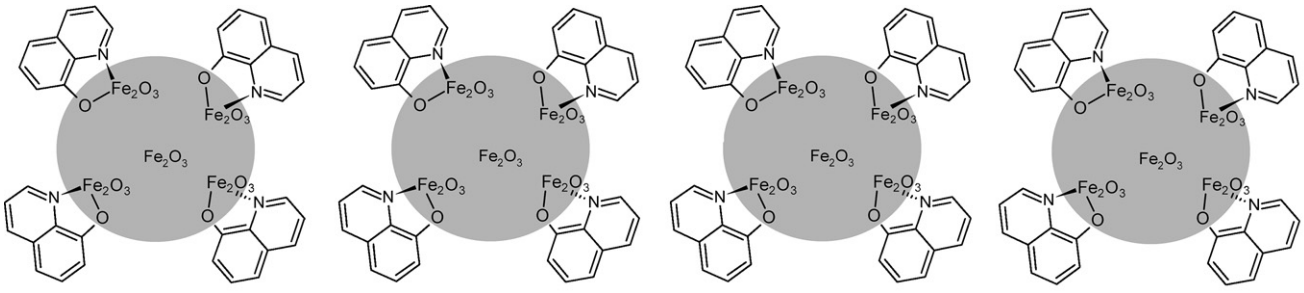


Fig. 3. Proposed structures of coated ferric oxide nanoparticles with 8-hydroxyquinoline.

3. Results and discussion

The main purpose of this work has been the investigation of the applications of ferric oxide nanoparticles with different surface area and particle size characteristics on chemiluminescent reactions and their use in analytical applications. It has been known that most of CL reactions proceed in the solutions; therefore, it was necessary to find techniques to bring initially the solid ferric oxide nanoparticles into a "pseudo-water-soluble" form and then apply them to CL reactions. For this purpose, different organic compounds with relatively good "affinity" to iron, such as nitrilotriacetic acid, 2,2-dipyridine, *o*,*o*-phenanthroline, 8-hydroxyquinoline and polyethylene glycols of various molecular weights were tested. 8-Hydroxyquinoline found to be the best reagent for the light reaction of luminol with hydrogen peroxide due to its highest effect on the enhancement and acceleration of the luminol light signals. As mentioned in Section 2, the colloidal solutions of ferric oxide nanoparticles were simply prepared by sonication of suspended solid ferric oxides in aqueous alkaline solutions of 8-hydroxyquinoline. The existence of ferric oxide nanoparticles in the colloidal solutions as well as the sizes and shapes of the nanoparticles were confirmed by TEM microscopy. The samples of coated ferric oxide nanoparticles with 8-hydroxyquinoline used for TEM analysis were obtained by transferring the supernatant of freshly prepared colloidal solutions into a centrifugation tube and subsequent centrifugation for 30 min at 6000 rpm. In most cases, this procedure yielded negligible amount of the precipitated material. By repeating the whole procedure many times and washing the precipitated solid material with ethanol, to remove surplus of 8-hydroxyquinoline and sodium hydroxide, enough material could be collected and subjected to TEM analysis. As representative samples for TEM analyses were chosen the catalyst No. 1 containing large particles (hematite, 20–40 nm) and catalysts No. 6, No. 7 and No. 9 having the smallest particles size with large surface areas (Table 1). The best TEM images were obtained in the case of the sample No. 1, where, in contrary to the initial non-coated sample (Fig. 1a), a core–shell structure of the nanoparticles coated with 8-hydroxyquinoline is clearly visible (Fig. 1b). Less visible is the coating of ferric oxide nanoparticles in the TEM images of catalysts No. 6, No. 7 and No. 9 (Fig. 2a–c).

Nevertheless, these images suggest the existence of the iron oxide nanoparticles in the solutions. Their size and morphological characteristics remain the same as those corresponding to the original iron oxides used for the colloidal solutions. In addition to TEM analysis, the adsorption of 8-hydroxyquinoline on the surface of ferric oxide nanoparticles was verified by FT-IR spectroscopy. The characteristic bands of 8-hydroxyquinoline at 1120 (C–O) and 1560 cm^{-1} (C=N) were shifted on the spectrum of coated material to 1180 (C–O) and 1615 (C=N), respectively, showing that the coordination occurs through nitrogen and oxygen of 8-hydroxyquinoline. The content of iron in the colloidal solution of sample No. 6 (solution A) was found to be 7.5 ± 0.8 ppm ($n = 5$) by atomic absorption spectroscopy.

The coating of ferric oxide nanoparticles with 8-hydroxyquinoline over five-membered chelate complexes is presented in Fig. 3. The adsorption of organic material to ferric oxide nanoparticles can also be achieved by other forces, such as van der Waals or electrostatic forces between organic material and ferric oxides. Such explanations have been suggested by other authors for stable iron oxides both in acidic and in alkaline solutions [28–30]. The hydrophobic aromatic compound bound on the surface of ferric oxide nanoparticles makes the whole complex more hydrophobic in aqueous solutions.

At this point, it should be noted that the novel coated catalysts are stable and transparent for about 5 days. After that time they form solid aggregates and precipitate in the alkaline aqueous solutions. These precipitates were not further examined because they were not relevant to CL measurements. All CL measurements were performed directly after preparation of the colloidal solutions. The stability of ferric oxide catalyst No. 6 is manifested by measuring the intensity–time profiles of the light reaction of luminol and hydrogen peroxide in different days. As shown in Fig. 4, the reaction kinetic profiles of the catalyzed luminol reaction change after the fifth day.

The catalytic activity of all prepared colloidal solutions of ferric oxide nanoparticles on the chemiluminescence reaction of luminol and hydrogen peroxide is shown in Table 1 and Fig. 5. Catalyst No. 6 shows the highest CL intensity enhancement compared to the blank reaction (up to 18-fold) and accelerates the reaction time up to 86-fold (Table 1 and Fig. 5). Therefore, this catalyst used for all CL applications. The blank reaction of luminol reaches

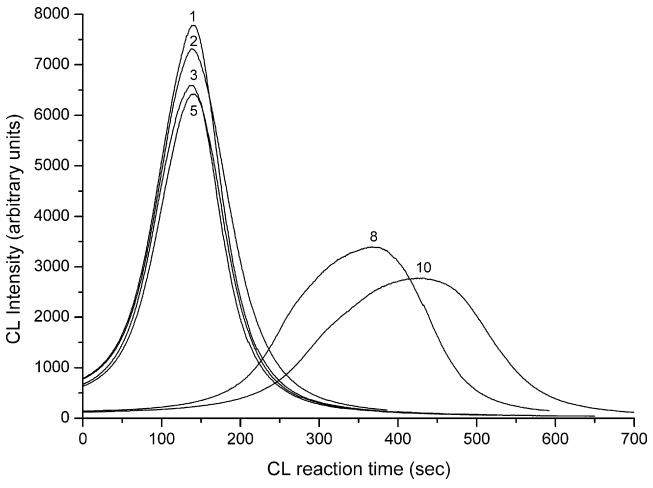


Fig. 4. Intensity–time profiles of the luminol light reaction with hydrogen peroxide catalyzed by ferric oxide No. 6 measured at different days.

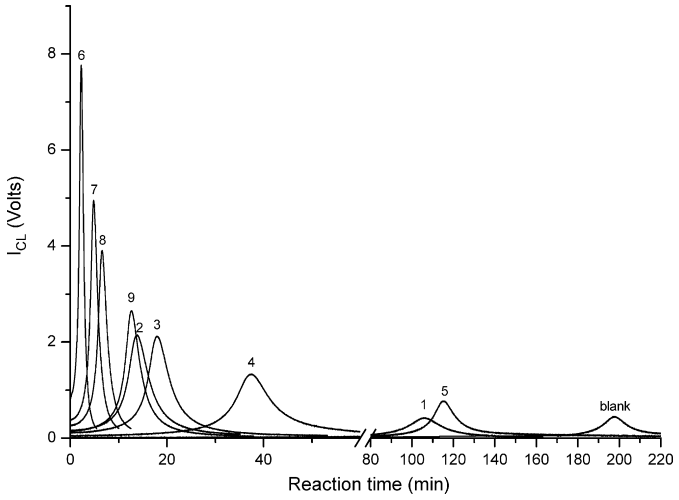


Fig. 5. CL reaction profiles of the luminol reaction with hydrogen peroxide in the presence and absence (blank reaction) of colloidal solutions of ferric oxide nanoparticles (the numbers on the peaks are referred to ferric oxides given in Table 1).

its intensity maximum after 197.6 ± 17.4 min with an intensity of 447.4 ± 30.2 mV (mean value of five measurements). At this point, it should be noted that the CL kinetic profile of the luminol reaction with hydrogen peroxide in the presence of ferric or ferrous ions of concentrations about 7.5 ppm is different with negligible intensity. Consequently, iron ions do not seem to be dissolved in the 8-hydroxyquinoline solution.

A more careful observation of Table 1 reveals that ferric oxide nanoparticles with relatively high surface areas (250–400 m^2/g) exhibit higher CL intensities (entries 6–8) than catalysts with smaller surface areas (20–43 m^2/g) (entries 1–4 and 9). Less significant enhancement on the CL intensity of the luminol CL reaction was observed by using ferric oxide particles of micrometer size (entry 5). Similar results were obtained for the acceleration of the luminol CL reaction. Namely, catalysts 6–8 accelerate the reaction time 1.85- to 86-fold while catalysts 1–4 and 9 only 5- to 12-fold. Again, much less significant acceleration of the CL reaction was observed by micrometer-sized ferric oxides (1.4-fold). The above results are reasonable due to the higher concentrations of organic and inorganic reagents adsorbed on the surface of catalysts with high surface areas. As the CL intensities are normally proportional to the concentration of all reagents involved in these reactions and as the hydrogen peroxide decomposition on the surface of metal oxide catalysts is accelerated, all these events might contribute to the obvious enhancement and acceleration of the luminol CL reaction in the presence of ferric oxide nanoparticles.

The CL intensities given in Table 1 are the results of optimized reaction conditions. Optimization experiments showed that the intensity of light signals increased linearly by increasing luminol and hydrogen peroxide concentrations up to 5.0×10^{-5} and 0.1 M, respectively, in the presence of 7.5 ppm catalyst No. 6. At higher concentrations, the instrument response was overloaded and the measurements could not proceed.

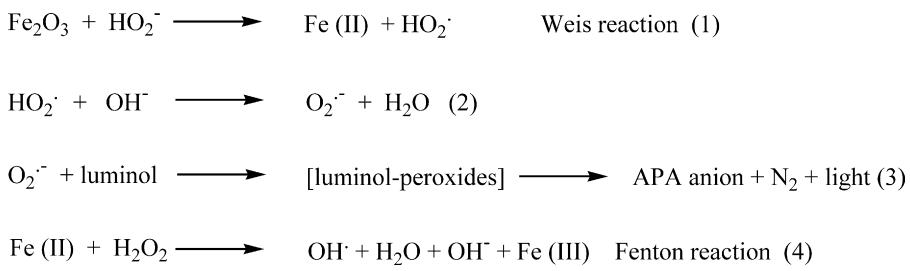
Using the optimized concentration of luminol (5×10^{-5} M) and catalyst No. 6 (7.5 ppm), the hydrogen peroxide was determined down to 1.25×10^{-3} M (S/N = 3). The calibration graph is linear in the range 2.0×10^{-3} to 0.1 M. The relative standard deviations at the concentration levels of 2.0×10^{-3} and 2.0×10^{-2} M hydrogen peroxide were 6.2 and 4.9%, respectively ($n = 5$). The linear regression equation and analytical characteristics were $\log CL_{Intensity} = 5.21\ (\pm 0.20) + 1.45\ (\pm 0.09) \log C$; $r^2 = 0.99$, $n = 5$, $Sy/x = 0.164$ and $P = 0.0006$. The detection limit of hydrogen peroxide found by this method is higher than other reported assays, such as spectrophotometric [31], chromatographic [32], electrochemical [33,34] and chemiluminescent techniques [35–38]; however, the simple instrumentation makes this method an attractive alternative.

The enhanced light signals of luminol–hydrogen peroxide reaction catalyzed by ferric oxide catalyst No. 6 was further tested for the estimation of hydrogen peroxide scavenging activity (IC-50 and TC-50) of some selected antioxidant compounds. This has been done by measuring either the reduction of chemiluminescent intensity or retardation of the reaction time of the corresponding blank reaction in the presence of various antioxidant concentrations. The blank reaction in these CL measurements is constituted from a mixture of 200 μL luminol solution B, 200 μL hydrogen peroxide (0.1 M), 200 μL colloidal catalyst No. 6 solution A and 200 μL aqueous sodium hydroxide solution (0.1 M) containing 0.1% (w/v) 8-hydroxyquinoline. As indicator for the estimation of hydrogen peroxide scavenging activity of selected antioxidants was chosen the concentration of antioxidants which reduces the light intensity of blank reaction to 50% (IC-50) or increases the reaction time of blank to 50% (TC-50). The IC-50 and TC-50 values of antioxidants were calculated from corresponding linear regression equations $AA_I\ (\%) = a + bC$ or $AA_T\ (\%) = a + bC$ using the corresponding a and b values and setting AA_I and AA_T equal to 50. Antioxidant activities at different antioxidant concentrations were calculated from the equations $AA_I\ (\%) = [(I_0 - I)/I_0] \times 100$ or $AA_T\ (\%) = [(T - T_0)/T_0] \times 100$, where I_0 and T_0 are the light intensity and reaction time of the blank (without antioxidant), and I and T the light intensities and reaction times of the samples, respectively. As the hydrogen peroxide scavenging activity of selected compounds varied largely, different concentrations were used to establish correlations between scavenging activity and concentration. The ranges, coefficients of determination (r^2), standard deviations of regression (Sy/x, $n = 5$) as well as the y-intercept (a) and slope (b) values of the corresponding linear regression equations, regarding the chemiluminescence intensity measurements, are given in Table 2. The estimated scavenging activities (IC-50 and TC-50) are given in Table 3.

It turns out that phenolic compounds with one hydroxyl group (tyrosol) or two hydroxyl groups on the aromatic ring (catechin and caffeic acid) exhibit higher hydrogen peroxide scavenging activities than those phenolic compounds with three hydroxyl groups (gallic and pyrrogallic acid). Weak scavenging activity was also observed for non-phenolic compounds, such ascorbic acid, vitamin E and the amino acid cysteine. The hydrogen peroxide scavenging activity of phenolic compounds measured by the present method is lower than those reported in other methods [39–47]. It can be said that this was in someway partially expected. It is known that comparison of antioxidant activities of organic compounds is a difficult task, especially if different reactive species are to be blocked in different methods. In most reported methods, the reactive species to be blocked are reactive free radicals, such as diphenylpicrylhydrazyl (DPPH), superoxide, peroxy- and hydroxyl radicals [39–47], and not relative stable neutral molecules such as hydrogen peroxide. Why trihydroxylated phenols exhibit lower scavenging activity than dihydroxylated ones is not easy to answer. Possibly, parts of the trihydroxylated phenols build stable complexes with ferric oxide nanoparticles or build side products which do not react with hydrogen peroxide, thus leading to reduced antioxidant properties.

Comparing the results of Table 3, it can be seen that both parameters of the novel catalyzed CL reactions, i.e. the decrease in the light intensity (IC-50) or retardation of the reaction time (TC-50), show similar results and can be used simultaneously for the estimation of hydrogen peroxide scavenging activity.

Regarding the CL mechanism of catalyzed luminol reaction with hydrogen peroxide in the presence of ferric oxide nanoparticles,



Scheme 1. Proposed CL mechanism of the catalyzed luminol reaction with hydrogen peroxide in the presence of ferric oxide nanoparticles.

we assume that this is similar to that proposed by Merenyi et al. for the non-catalyzed luminol reaction [48,49], but with the difference that hydrogen peroxide is initially broken up, in a Weis-like reaction on the surface of ferric oxide nanoparticles, into superoxide radical anion, which on a reaction with luminol gives light and 3-aminophthalic acid (APA) anion (Scheme 1). The scavenging mechanism of hydrogen peroxide by phenolic compounds is not exactly known. It is assumed that phenols in competition reactions to luminol react with the intermediary produced superoxide radical anion ($O_2^{\bullet -}$) and decrease the light signals.

4. Conclusions

In this work, we have shown that colloidal solutions of ferric oxide nanoparticles can easily be prepared at room temperature by simple sonication of suspended solid nanoparticles and 8-hydroxyquinoline in alkaline aqueous solution. Application of these relative stable colloidal solutions in the CL reaction of luminol with hydrogen peroxide improves its CL intensities up to 18-fold and accelerates the reaction times up to 86-fold. The enhanced CL signals were used for the quantification of hydrogen peroxide in concentrations down to 1.25×10^{-3} M as well as for the estimation of hydrogen peroxide scavenging activities of organic antioxidants, with best results for mono- and dihydroxylated phenols.

Acknowledgements

The authors wish to thank the General Secretaries of Research and Technology of Greece and Czech Republic as well as the National Centre for Scientific Research "Demokritos" for funding this bilateral project.

References

[1] Y. Su, H. Chen, Z. Wang, Y. Li, Appl. Spectrosc. Rev. 42 (2007) 139–176.
[2] C.A. Marquette, L.G. Blum, Anal. Bioanal. Chem. 385 (2006) 546–555.
[3] A. Roda, M. Guardigli, P. Pasini, M. Miracoli, E. Michelini, M. Musiani, Anal. Chim. Acta 541 (2005) 25–35.
[4] Z.Y. Zhang, S.C. Zhang, X.R. Zhang, Anal. Chim. Acta 541 (2005) 37–47.
[5] A.M. Garcia-Campana, W.R.G. Baeyens (Eds.), Chemiluminescence in Analytical Chemistry, Marcel Dekker, Inc., 2000.
[6] A. Roda, P. Pasini, M. Mirasoli, E. Nichelini, M. Guardagli, Trends Biotechnol. 22 (2004) 295–303.
[7] M. Catala Icardo, L. Lahuerta Zamora, G.M. Anton-Fos, J. Martinez Calatayud, M.J. Duart, Trends Anal. Chem. 24 (2005) 782–791.
[8] X. Wang, J. Wang, N. Yang, Food Chem. 102 (2007) 422–426.
[9] L. Gamiz-Gracia, A.M. Garcia-Campana, J.J. Soto-Chinchilla, J.F. Huertas-Perez, A. Gonzalez-Casado, Trends Anal. Chem. 24 (2005) 927–942.
[10] K. Motyka, P. Mikuska, Z. Vecera, Anal. Chim. Acta 562 (2006) 236–244.
[11] M.H. Chowdhury, K. Aslan, N. Malyn, J.R. Lakowicz, C.D. Geddes, J. Fluoresc. 16 (2006) 295–299.
[12] L.J. Kricka, G.H.G. Thorpe, R.A.W. Stott, Pure Appl. Chem. 59 (1987) 651–654.
[13] R. Iwata, T. Hayashi, Y. Nakao, M. Yamaki, T. Yoshimasa, H. Ito, Y. Saito, M. Mukoyam, K. Nakao, Clin. Chem. 42 (1996) 1155–1158.
[14] A.D. Ilyina, J.L. Martínez-Hernández, B.H. López-Luján, J.E. Mauricio-Benavides, J. Romero-García, J. Rodríguez-Martínez, Appl. Biochem. Biotechnol. 88 (2000) 45–58.
[15] H. Chen, F. Gao, R. He, D. Cui, J. Colloid Interf. Sci. 315 (2007) 158–163.
[16] Y. Li, P. Yang, P. Wang, L. Wang, Anal. Bioanal. Chem. 387 (2007) 585–592.
[17] B.A. Gorman, P.S. Francis, D.E. Dunstan, N.W. Barnett, Chem. Commun. (2007) 395–397.
[18] Z.F. Zhang, H. Cui, C.Z. Lai, L.J. Liu, Anal. Chem. 77 (2005) 3324–3329.
[19] H. Cui, Z.F. Zhang, M.J. Shi, J. Phys. Chem. B 109 (2005) 3099–3103.
[20] S.-L. Xu, H. Cui, Luminescence 22 (2007) 77–87.
[21] Y. Zhu, J. Shi, Z. Zhang, C. Zhang, X. Zhang, Anal. Chem. 74 (2002) 120–124.
[22] L. Zhengping, F. Cui, Chem. J. Internet 7 (2005) 59–66, http://www.cemistrymag.org/cji/2005/079059pe.htm.
[23] S.-S. Lin, M.D. Gurol, Environ. Sci. Technol. 32 (1998) 1417–1423, and references cited therein.
[24] H.-H. Huang, M.-C. Lu, J.-N. Chen, Water Res. 35 (2001) 2291–2299, and references cited therein.
[25] A.A. Lysova, A.O. Kuz'min, V.N. Parmon, Kinet. Catal. 44 (2003) 86–90.
[26] R. Zboril, L. Machala, M. Mashlan, V. Sharma, Cryst. Growth Des. 4 (2004) 1317–1325.
[27] M. Hermanek, R. Zboril, I. Medrik, J. Pechousek, C. Gregor, J. Am. Chem. Soc. 129 (2007) 10929–10936.
[28] E. Tombacz, A. Majzik, Z.S. Horvat, E. Illes, Romanian Rep. Phys. 58 (2006) 281–286.
[29] S. Wan, Y. Zheng, Y. Liu, H. Yan, K. Liu, J. Mater. Chem. 15 (2005) 3424–3430.
[30] C. Yee, G. Kataby, A. Ulman, T. Prozorov, H. White, A. King, M. Rafailovich, J. Sokolov, A. Gedanken, Langmuir 15 (1999) 7111–7115.
[31] E.M. Elnemma, Bull. Korean Chem. Soc. 25 (2004) 127–129.
[32] K. Kobayashi, S. Kawai, J. Chromatogr. A 245 (1982) 339–345.
[33] A. Iwase, S. Kudo, N. Tanaka, Anal. Chim. Acta 110 (1979) 157–160.
[34] J. Hrbac, V. Halouzka, R. Zboril, K. Papadopoulos, T. Triantis, Electroanalysis 19 (2007) 1850–1854.
[35] S. Hanaoka, J.M. Lin, M. Yamada, Anal. Chim. Acta 426 (2001) 57–64.
[36] B. Li, Z. Zhang, L. Zhao, Anal. Chim. Acta 445 (2001) 161–167.
[37] O. Nozaki, H. Kawamoto, Anal. Chim. Acta 495 (2003) 233–238.
[38] J.-M. Lin, X. Shan, S. Hanaoka, M. Yamada, Anal. Chem. 73 (2001) 5043–5051.
[39] Z. Sroka, W. Cisowski, Food Chem. Toxicol. 41 (2003) 753–758.
[40] M.A. Soobrattee, V.S. Neergheen, A. Luximon-Ramma, O.I. Aruoma, T. Bahorun, Mutat. Res. 579 (2005) 200–213.
[41] P. Cos, P. Rajan, I. Vedernikova, M. Calomme, L. Pieters, A. Vlietinck, K. Augustins, A. Haemers, D. Vandenberghe, Free Radic. Res. 36 (2002) 711–716.
[42] O. Hirayama, M. Takagi, K. Hukumoto, S. Katoh, Anal. Biochem. 247 (1997) 237–241.
[43] C. Siquet, F.A. Martins, J.C. Lima, S. Reis, F. Borges, Free Radic. Res. 40 (2006) 433–442.
[44] T. Triantis, A. Stelakis, D. Dimotikali, K. Papadopoulos, Anal. Chim. Acta 536 (2005) 101–105.
[45] A. Mansouri, D. Makris, P. Kefalas, J. Pharm. Biomed. Anal. 39 (2005) 22–26.
[46] S. Son, B.A. Lewis, J. Agric. Food Chem. 50 (2002) 468–472.
[47] M. Arts, J.S. Dallinga, H.-P. Voss, G. Haenen, A. Bast, Food Chem. 80 (2003) 409–414.
[48] G. Merenyi, J.S. Lind, T.E. Eriksen, J. Biolumin. Chemilumin. 5 (1990) 53–56.
[49] G. Merenyi, J.S. Lind, J. Am. Chem. Soc. 102 (1980) 5830–5835.