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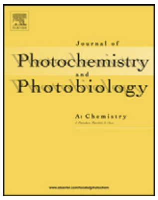

Platinum nanoparticle-catalyzed lucigenin–hydrazine chemiluminescence

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It was found that lucigenin alkaline solution could react with hydrazine in the presence of Pt nanoparticles to generate strong chemiluminescence (CL) centered at 480 nm. In order to explore the CL mechanism, UV–visible spectra, X-ray photoelectron spectra studies before and after the CL reaction were carried out. The effects of O_2 and superoxide dismutase (SOD) on the CL reaction were examined. The catalytic effect of Pt NPs on the hydrazine–O_2 reaction was studied. A possible mechanism is proposed to be due to that Pt NPs catalyzed the reaction between hydrazine and the dissolved oxygen under alkaline conditions to yield hydroperoxide species and superoxide radical anion, which further oxidized lucigenin to produce CL emission. Moreover, the effects of some organic compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO), amino (NH_2), or sulfur groups on the lucigenin–hydrazine–Pt NPs CL system were tested. Thiol-containing compounds such as cysteine (Cys), glutathione (GSH), homocysteine (Hcy), and 6-mercaptopurine (6-MP) were observed to greatly enhance the CL intensity. It is suggested that the CL enhancement might be due to the fact that thiol-containing compounds could facilitate the electron transfer process under the catalysis of Pt nanoparticles and accelerate the generation of $OH^\bullet$ and $O_2^{\bullet-}$ radicals, leading to the strong CL.

1. Introduction

In recent years, metal nanoparticle (NP)-involved chemiluminescence (CL) has received considerable interest because of their unique chemical reactivity, catalytic properties and surface property [1]. For example, metal NPs such as Au NPs, Ag NPs and Pt NPs can participate in CL reactions as reductants, catalysts, luminophors and nano-sized reaction platforms. Among them, metal NPs-catalyzed CL has become an important subject. It has been reported that Au NPs, Ag NPs and Pt NPs could catalyze the luminol–H_2O_2 CL reaction [2–4]. Au NPs and Ag NPs could catalyze the luminol–ferricyanide CL reaction [5,6], and Au NPs could catalyze the luminol–$AgNO_3$ CL reaction and luminol–hydrazine CL reaction [7,8]. It was also found that Au–Ag alloy nanoparticles could catalyze the Rhodamine 6G-Cerium(IV) CL reaction [9]. However, for metal nanoparticle as CL catalysts, the used metal NPs are focused on Au NPs and Ag NPs, and other metal NPs are rarely studied. Besides, the studied CL system is mainly limited to luminol reactions. For other famous CL reactions such as lucigenin CL reactions, metal NPs seem to be inefficient for catalysis. There are few reports about catalysis of metal NPs in lucigenin CL reactions. Recently, it was found that ethanol can initiate Pt NPs to catalyze the lucigenin CL reaction in an alkaline solution, leading to a visible light emission with autocatalytic property [10]. The CL emission was also time-tunable by adjusting the concentration of Pt NPs injected. Both Pt NPs and ethanol were necessary for autocatalytic CL. Pt NPs were general catalysts for the oxidation of ethanol to acetaldehyde and the CL enhancement by acetaldehyde. Ethanol in this system was an initiator for catalysis.

In the present study, it was found that Pt NPs could directly catalyze the reaction of lucigenin with hydrazine in an alkaline solution, accompanying with a strong CL. The effects of Pt NPs with different protecting agents synthesized by the citrate on the lucigenin–hydrazine CL system were explored. UV–visible spectra and X-ray photoelectron spectra (XPS) studies were conducted before and after the CL reaction. The effects of O_2 and superoxide dismutase (SOD) on the CL reaction were examined. The catalytic effect of Pt NPs on the hydrazine–O_2 reaction was studied. A possible CL mechanism is proposed. Moreover, the effects of 30 organic compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO), amino (NH_2), or sulfur groups on the lucigenin–hydrazine–Pt NPs CL system were explored. It was found that thiol-containing compounds could greatly enhance the CL. The CL enhancing mechanism is discussed.

2. Experimental

2.1. Chemicals and solutions

Lucigenin was obtained from TCI (Japan). Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 37.0%, w/w), trisodium citrate ($Na_3C_6O_7$), NaOH, poly-(vinylpyrrolidone) (PVP, MW 36000), hydrazine

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($N_2H_4{\cdot}H_2O$), NaCl, hydrogen peroxide (H_2O_2), superoxide dismutase (SOD), horseradish peroxidase (HRP), and 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) were obtained from Shanghai Reagent Co., Ltd (Shanghai, China). 6-Mercaptopurine (6-MP), adenine, tripropylamine, ethylenediamine, adrenaline, norepinephrine, aniline, o-diaminobenzene, m-phenylenediamine, p-phenylenediamine, phenol, catechol, resorcinol, hydroquinone, methanol, ethanol, acetaldehyde, and formic acid were purchased from Sangon Biological Engineering Technology & Services Co., Ltd. (Shanghai, China). Homocysteine (Hcy), glutathione (reduced) (GSH), cysteine (Cys), cystine, glutathione (oxidized) (GSSG), glycine (Gly), histidine (His), tryptophan (Trp), arginine (Arg), and methionine (Met) were obtained from Solarbio (Beijing, China). All the reagents were of analytical grade, and Milli-Q water (18.2 MΩ) (Millipore, USA) was used throughout.

The stock solution of lucigenin (1.0×10^{-3} mol/L) was prepared by dissolving lucigenin in water. Working solutions of lucigenin were prepared by diluting the stock solution with water. The stock solution of (1.0×10^{-3} mol/L) 6-MP was prepared in 0.01 mol/L NaOH and stored in 4 °C. Working solutions of 6-MP were prepared by diluting appropriate amount of stock solution with water and stored at 4 °C in the dark during the day.

2.2. Synthesis of citrate- and PVP-protected Pt colloids by the citrate reduction method

The citrate-protected colloidal platinum nanoparticles were prepared as described by Henglein et al. [11]. The procedure is as follows: $H_2PtCl_6{\cdot}6H_2O$ (0.03 mmol) was added to 50 mL water and heated to boiling with stirring in a 100 mL round-bottomed flask. After adding 5.0 mL trisodium citrate (1.0% aqueous solution), the resulting solution was maintained at boiling for 1 h. Brown-colored colloidal platinum colloids were then obtained and cooled to room temperature. PVP-protected Pt NPs were prepared by the citrate reduction method according to the same procedure as above, except for 33 mg PVP (0.3 mmol as monomeric unit) was added as a protective agent.

2.3. Chemiluminescence measurements

The chemiluminescence detection was conducted on a laboratory-built flow injection chemiluminescence system, consisting of a model IFFM-D flow injection system (Ruimai Electronic Science Co.), a model IFFS-A luminometer, and a computer, as shown in Fig. 1. Water carrying the colloidal solution of Pt NPs was mixed with hydrazine and then with NaOH–lucigenin solutions. The CL signals were monitored by the PMT adjacent to the flow CL cell. When the CL system was used to study the effect of organic compounds, the sample solution containing organic compounds and the Pt colloids were mixed offline, which was combined with hydrazine and then with NaOH–lucigenin solutions. The value of $\Delta I = I - I_0$ showed the effect of organic compounds on the CL intensity of lucigenin–hydrazine–Pt NPs system, where I_0 stands for the signal in the absence of organic compounds and I stands for the signal in the presence of organic compounds.

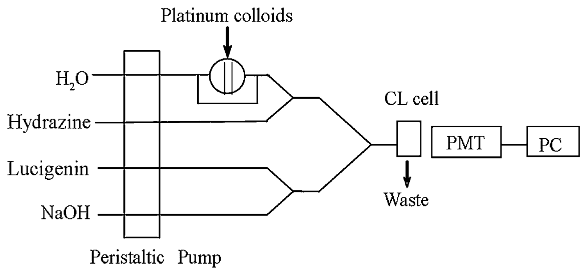

Fig. 1. Schematic diagram of flow-injection CL detection system.

2.4. Optical measurements

CL spectra and fluorescence spectra were conducted on a model F-7000 Fluorescence Spectrophotometer (Hitachi, Japan). UV–visible spectra and X-ray photoelectron spectra were carried out on a model UV-8453 UV–visible spectrometer (Agilent, USA) and on a model ESCALAB MK II electron spectrometer (VG, England). The XPS sample was prepared as follows: NaCl was added to a 100 mL Pt NPs to precipitate the particles, then, the mixture was centrifuged and the precipitates obtained were thoroughly washed by water.

3. Results and discussion

3.1. Platinum colloids-involved lucigenin CL

When water carrying the colloidal solution of Pt NPs protected by citrate was mixed with hydrazine and then with NaOH–lucigenin solution, a strong CL emission was observed as shown in Fig. 2, curve a. The CL intensity was even comparable with that of well-known lucigenin–H_2O_2 system. In the absence of colloidal Pt nanoparticles, only a weak CL was observed from the baseline of curve a. To exclude the effect of the concomitants in the experiment, Pt colloids were centrifuged at 12,000 rpm for 30 min, the obtained supernatant instead of Pt colloids was injected into the CL system and no obvious CL signal was observed as shown in Fig. 2, curve c. Therefore, the CL was related to the Pt NPs.

The effects of platinum colloids protected by different reagents on the lucigenin–hydrazine CL system were also investigated. As shown in Fig. 2, curves b and c, the CL intensity with platinum colloids protected by citrate (Fig. 2, curve a) was stronger than that with platinum colloids protected by PVP (Fig. 2, curve b).

The CL spectra for the platinum colloids–lucigenin–hydrazine system were studied as shown in Fig. 2, inset. The result demonstrated that the maximum emission wavelength was at 480 nm, which was in good agreement with the emission of the typical lucigenin system, revealing that the luminophor was still the excited state N-methylacridone (NMA) [12]. Therefore, the addition of platinum colloids did not lead to the generation of new luminophor.

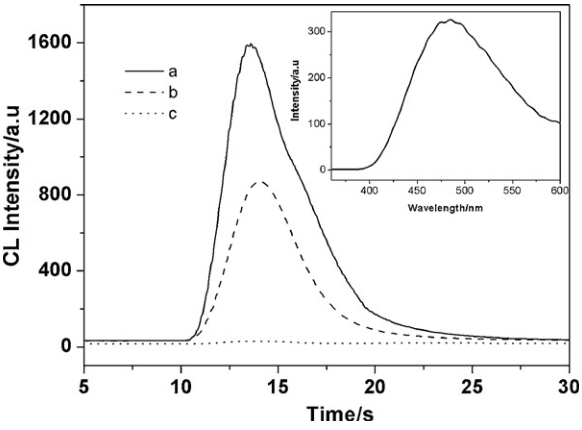

Fig. 2. CL profiles when Pt NPs were injected into hydrazine, then combined with the mixture of lucigenin and NaOH. (a) citrate-protected Pt; (b) PVP-protected Pt; (c) blank (the supernatant of the citrate-protected Pt NPs after centrifugation). Conditions: lucigenin, 5×10^{-6} mol/L; NaOH, 0.1 mol/L; hydrazine, 0.01 mol/L; Pt NPs, 1.5 μmol/L. The inset is the CL spectra.

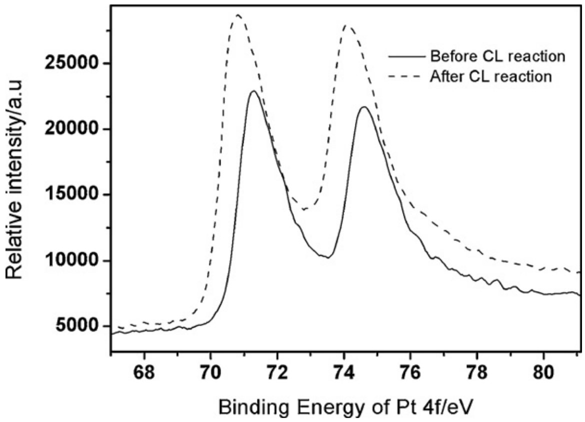

Fig. 3. XPS of citrate-protected Pt NPs before and after CL reaction.

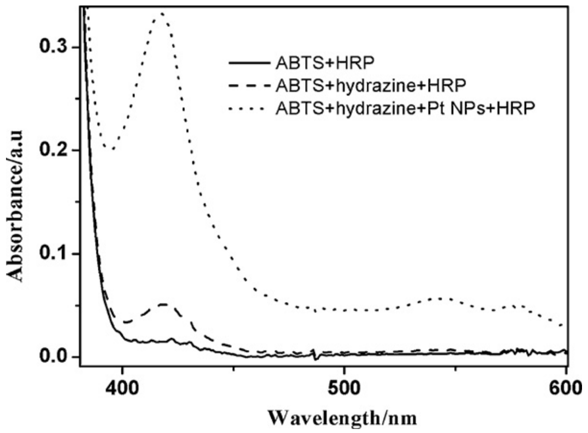

Fig. 5. UV–visible absorption spectra of ABTS + HRP (solid line), ABTS + hydrazine + HRP (dashed line) and PtNPs + ABTS + hydrazine + HRP (dotted line). Final concentration of each reagent: ABTS, 5×10^{-4} mol/L; hydrazine, 0.01 mol/L; HRP, 10^{-4} mol/L; Pt NPs, 15 μmol/L.

3.2. Possible mechanism of platinum colloids-involved lucigenin CL reaction

The CL mechanism for the Pt NPs–lucigenin–hydrazine system was explored. XPS studies were conducted to investigate the surface state of Pt NPs before and after the CL reaction as shown in Fig. 3. Before the CL reaction, the binding energies of Pt ($4f_{7/2}$) and Pt ($4f_{5/2}$) electrons in the high-resolution spectrum of the Pt 4f line were 71.3 and 74.6 eV, respectively, indicating that the Pt particles were in the Pt (0) state. After the CL reaction, the binding energies of Pt 4f were found to undergo a small change (the binding energies of Pt ($4f_{7/2}$) and Pt ($4f_{5/2}$) were 70.8 and 74.1 eV). A slightly higher binding energy (∼0.5 eV) was observed for Pt ($4f_{7/2}$) and Pt ($4f_{5/2}$) electrons, indicating that the surface state of Pt NPs did change slightly after the CL reaction. However, such a small difference (∼0.5 eV) in binding energy after and before the CL reaction could not lead to a change in the oxidation state of Pt NPs. In conclusion, the shape and size of Pt NPs did not change before and after the CL reaction and the CL may originate from the catalytic effect of Pt NPs.

The effect of oxygen on the CL reaction was also studied. When nitrogen was bubbled into the reaction solutions, the CL intensity declined to a great extent (Fig. 4). It should be noted that the bubbling of nitrogen could reduce the oxygen concentration in the reaction solution, but a completely oxygen-free solution could not be achieved. This result revealed that oxygen was involved in the CL process.

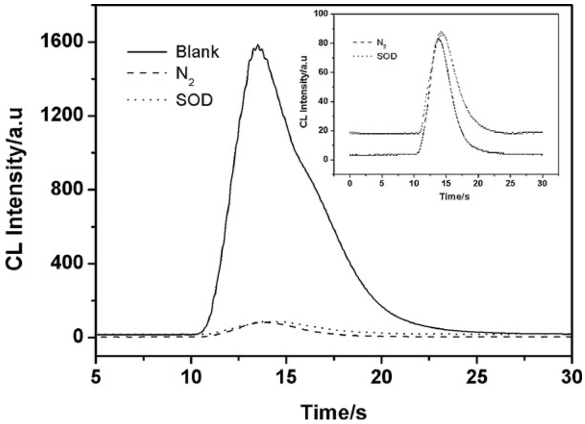

Fig. 4. Effect of N_2 and SOD on lucigenin–hydrazine–Pt NPs CL reaction. From top to bottom: lucigenin–NaOH–hydrazine–Pt NPs, N_2–lucigenin–NaOH–hydrazine–Pt NPs, SOD–lucigenin–NaOH–hydrazine–Pt NPs. Conditions: lucigenin, 5×10^{-6} mol/L; NaOH, 0.1 mol/L; hydrazine, 0.01 mol/L; SOD, 200 U/mL; Pt NPs, 1.5 μmol/L. The inset is the enlarged segment.

Furthermore, superoxide dismutase (SOD) is known to be a scavenger of superoxide radical anions [13]. When SOD was added into the Pt NPs–lucigenin–hydrazine system (Fig. 4), the CL decreased obviously, supporting that superoxide anion took part in the CL reaction.

Earlier work demonstrated that Au NPs could catalyze the reaction of hydrazine with dissolved oxygen to form H_2O_2 [8]. Thus it was deduced that Pt NPs might also catalyze the reaction of hydrazine with dissolved oxygen to form H_2O_2. It was reported that ABTS could be oxidized by hydrogen peroxide by virtue of horseradish peroxidase (HRP) catalysis, leading to an increase in absorbance at 420 nm due to the oxidation of ABTS [14]. Accordingly, whether or not Pt NPs can catalyze the formation of H_2O_2 by the reaction of hydrazine with O_2 can be examined by the H_2O_2–HRP–ABTS reaction. Fig. 5 showed that absorption spectra, the absorbance at 420 nm increased greatly and the amount of H_2O_2 was much higher than that in the absence of Pt NPs. This revealed that Pt NPs catalyzed the formation of H_2O_2 generated by the reaction of hydrazine with dissolved oxygen.

Aiuchi et al. [15] reported that Pt NPs as catalysts could transfer electrons to hydrogen peroxide to cause its decompose in weakly alkaline solutions, which usually led to the formation of $OH^\bullet$ radical via the radical chain mechanism [16,17]. $OH^\bullet$ radicals readily interact with H_2O_2 to yield superoxide radical anion ($O_2^{\bullet-}$) [18]. It is known that $O_2^{\bullet-}$ could react with lucigenin to produce light emission. Accordingly, the possible pathways for the CL reaction may be as follows:

$$2O_2(g) + N_2H_4(aq) \xrightarrow{\text{Pt NPs}} 2H_2O_2(aq) + N_2(g) \tag{1}$$

$$H_2O_2 \xrightarrow{\text{Pt NPs}} 2OH^\bullet \tag{2}$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \tag{3}$$

$$HO_2^\bullet + OH^- \rightarrow O_2^{\bullet-} + H_2O \tag{4}$$

$$O_2^{\bullet-} + Luc^{2+} \rightarrow O_2 + Luc^{\bullet+} \tag{5}$$

$$Luc^{\bullet+} + O_2^{\bullet-} \rightarrow LucO_2 \rightarrow NMA + NMA^* \tag{6}$$

The first step of CL reaction without Pt NPs was a slow reaction. The addition of Pt NPs could accelerate the formation of active oxygen-containing intermediates such as $OH^\bullet$ and $O_2^{\bullet-}$ to generate strong light emission. As a result, Pt NPs catalyzed the reaction

Table 1
Responds of 30 organic compounds to lucigenin–hydrazine–Pt NPs CL system.

Compounds[a]	CL variation[b] (%)	Compounds	CL variation (%)
Homocysteine	500	Noradrenaline	18.9
L-Glutathione(re)	350	Aniline	−25.1
L-Cysteine	326	o-Diaminobenzene	−47.1
6-MP	127	m-Phenylenediamine	−19.5
L-Cystine	35.8	p-Phenylenediamine	−10.1
L-Glutathione(ox)	31.4	Phenol	ND
L-Methionine	9.4	Catechol	ND
Glycine	13.2	Resorcinol	ND
Histidine	37.7	Hydroquinone	ND
Tryptophan	13.2	Phloroglucinol	ND
Arginine	15.1	Benzoic acid	ND
Tripropylamine	11.3	Methanol	ND
Ethylenediamine	12.6	Ethanol	ND
Adenine	13.5	Acetaldehyde	ND
Adrenaline	22.1	Formic acid	ND

[a] Working conditions: lucigenin, 5×10^{-6} mol/L; NaOH, 0.1 mol/L; hydrazine, 0.01 mol/L, Pt NPs, 1.5 μmol/L, organic compounds, 1×10^{-6} g/mL. ND, not detected.

[b] The CL variation percentage (average of three replicates) was calculated as $\Delta I/I_0 \times 100\%$, where $\Delta I = I - I_0$, I and I_0 stands for the CL signal in the presence and absence of organic compounds.

between hydrazine and the dissolved oxygen under alkaline conditions to yield $OH^{\bullet}$ and $O_2^{\bullet -}$, which further oxidized lucigenin to produce the excited state NMA, leading to CL emission.

3.3. *Effect of organic compounds*

The lucigenin–hydrazine–Pt NPs CL system has the advantages of low background and good stability. In order to evaluate whether or not the CL system is applicable for the detection of some compounds, the responds of 30 organic compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO), amino (NH_2), or sulfur groups with the concentration of 10^{-6} g/mL to this system were studied. The results are listed in Table 1, which showed that some of the tested compounds could inhibit or enhance the CL intensity to some extent. From these data, the following conclusions can be drawn:

1. Sulfur-containing compounds enhanced CL. The magnitude of enhancement is in following order: thiol-containing compounds (–SH) > disulfide-containing compounds (–S–S–) > sulfide-containing compounds (–S–).
2. Aniline and its derivatives, e.g. o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, inhibited CL.
3. Aliphatic amine compounds, e.g. glycine, histidine, tryptophan, arginine, ethylenediamine, tripropylamine, adenine, slightly enhanced CL.
4. Adrenaline and noradrenaline, which contained multiple functional groups such as hydroxyl (OH) and amino (NH_2), slightly enhanced CL.
5. The compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO) group, e.g. phenol, o-dihydroxybenzene, resorcinol, p-dihydroxybenzene, phloroglucinol, methanol, ethanol, acetaldehyde, benzoic acid, formic acid, did not showed obvious effects on the CL system.

The results demonstrated that the CL inhibition and enhancement might depend on the functional groups and the molecular structure. The responses of thiol-containing compounds such as Hcy, GSH, Cys and 6-MP toward the lucigenin CL involving Pt NPs are striking, which may be used to the detection of these compounds.

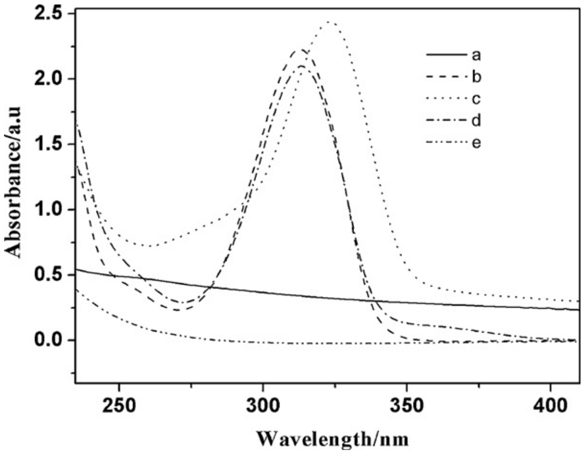

Fig. 6. UV–visible absorption spectra of 6-MP, Pt NPs, H_2O_2 and their mixture. (a) Pt NPs; (b) 6-MP; (c) 6-MP + PtNPs; (d) 6-MP + H_2O_2; (e) H_2O_2. Final concentration of each reagent: 6-MP, 2×10^{-5} mol/L; Pt NPs, 120 μmol/L; H_2O_2, 8 mmol/L.

The CL enhancement mechanism by thiol-containing compounds of Pt NPs–lucigenin–hydrazine system was explored. 6-MP was chosen as a model compound. The interactions between 6-MP and Pt NPs and among 6-MP, Pt NPs and H_2O_2 were studied. The UV–visible absorption spectra of 6-MP, Pt NPs, H_2O_2 and their mixtures are shown in Fig. 6. It could be seen that 6-MP had a notable absorption peak at 312 nm, Pt NPs and H_2O_2 had no obvious absorption peak. However, when 6-MP was mixed with Pt NPs, the UV–visible absorption peak of 6-MP shifted from 312 nm to 323 nm (Fig. 6, curve c). The results revealed that Pt NPs could interact with 6-MP, which is in good agreement with earlier work reported by Tang. They found that Pt NPs surface could be modified by alkylthiol compounds [19,20]. On the other hand, it is found that a slight decrease in 312 nm absorption peak when 6-MP mixed with H_2O_2 (Fig. 6, curve d), indicating that 6-MP could react with H_2O_2, which is in good agreement with earlier work reported by Zhou and Huang [21,22]. Furthermore, the UV–visible absorption spectra of the mixed solutions of 6-MP, H_2O_2 and Pt NPs were conducted as showed in Fig. 7. When 6-MP was mixed with H_2O_2 in the presence of Pt NPs, the intensity of typical absorption peak of 6-MP in 323 nm decreased with time, while the new absorption peak in 288 nm that ascribed to the oxidized product of 6-MP [23] increased (Fig. 7, curves b–e). It is possible that strong reaction between 6-MP and H_2O_2 happened in the presence of Pt NPs. As mentioned above, Pt NPs as catalysts could transfer electrons to hydrogen peroxide to produce $OH^{\bullet}$ [15], which readily attack thiol-containing

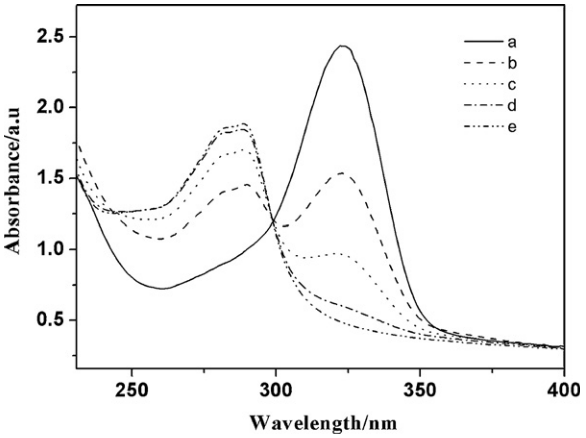

Fig. 7. UV–visible absorption spectra. (a) 6-MP + PtNPs; (b) 5 s after 6-MP + H_2O_2 + PtNPs reaction; (c) 10 s after 6-MP + H_2O_2 + PtNPs reaction; (d) 15 s after 6-MP + H_2O_2 + PtNPs reaction; (e) 30 s after 6-MP + H_2O_2 + PtNPs reaction. Final concentration of each reagent: 6-MP, 2×10^{-5} mol/L; Pt NPs, 120 μmol/L; H_2O_2, 8 mmol/L.

compounds (RSH) to form sulfide radical anion ($RS^•$) [24]. It is proposed that RSH could ionize to produce sulfide anion ($RS^−$), which could react with $RS^•$ to form disulfide radical anion ($RSSR^{•−}$) [25]. It was also reported that $RSSR^{•−}$ could transfer their unpaired electron to oxygen (O_2) to produce $O_2{}^{•−}$ and RSSR [26]. Moreover, RSSR can hydrolyze to RSOH and RSH. The RSOH may further hydrolyze to RSO_2H [27]. To determine the final products in the CL reaction, mass spectrometer is used to identify them. The results showed two obvious peaks (170.16 and 185.14) in the mass spectra, which are ascribed to $[RSH^•H_2O]^+$ and $[RSO_2H_2]^+$ respectively. Therefore, RSSR finally hydrolyzed to RSH and RSO_2H. It is known that $O_2{}^{•−}$ could react with lucigenin to produce light emission. Therefore, it is deduced that Pt NPs catalyzed the hydrazine–O_2 reaction to produce H_2O_2, followed by the formation of $OH^•$; $OH^•$ attacked 6-MP to produce disulfide radical anion ($RSSR^{•−}$), which reacted with the dissolved oxygen (O_2) to yield superoxide radical anion ($O_2{}^{•−}$); the further reaction of $O_2{}^{•−}$ with lucigenin led to light emission. The CL reaction in the presence of 6-MP may proceed as follow:

$$2O_2(g) + N_2H_4(aq) \xrightarrow{\text{Pt NPs}} 2H_2O_2(aq) + N_2(g) \quad (7)$$

$$H_2O_2 \xrightarrow{\text{Pt NPs}} 2OH^• \quad (8)$$

$$OH^• + RSH \rightarrow RS^• + H_2O \quad (9)$$

$$RSH \rightarrow RS^- + H^+ \quad (10)$$

$$RS^• + RS^- \rightarrow RSSR^{•-} \quad (11)$$

$$RSSR^{•-} + O_2 \rightarrow RSSR + O_2{}^{•-} \quad (12)$$

$$RSSR + H_2O \rightarrow RSOH + RSH \quad (13)$$

$$RSOH + 2OH^- \rightarrow RSO_2H + H_2O \quad (14)$$

$$O_2{}^{•-} + Luc^{2+} \rightarrow O_2 + Luc^{•+} \quad (15)$$

$$Luc^+ + O_2{}^{•-} \rightarrow LucO_2 \rightarrow NMA + NMA^* \quad (16)$$

The addition of thiol-containing compounds could facilitate the electron transfer process and accelerate the generation of $OH^•$ and $O_2{}^{•−}$ radicals by virtue of the catalysis of Pt NPs, lead to the strong CL. The reason for that the compounds containing disulfide (–S–S–) and sulfide (–S–) bond exhibited slight enhancement effects may be no free thiol groups in these compounds.

Because of weak interaction between $–NH_2$ group and Pt NPs and very weak interaction between the compounds containing –OH, –COOH and –CO– and Pt NPs [20], these compounds only showed slight effect or no effect on the Pt NPs–lucigenin–hydrazine CL system.

4. Conclusions

Pt NPs synthesized by the citrate reduction method could catalyze the lucigenin–hydrazine reaction, accompanying by a CL emission. The luminophor of this CL system was identified as the excited state NMA. The CL mechanism was suggested to be due to that Pt NPs catalyzed the reaction between hydrazine and the dissolved oxygen under alkaline conditions to yield superoxide radical anion, which further oxidized lucigenin to produce the excited state NMA, leading to light emission. The effects of 30 organic compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO), amino (NH_2), sulfur groups on this CL system were studied. Thiol-containing compounds were observed to greatly enhance the CL intensity. The CL enhancement is likely due to that Pt NPs catalyzed the hydrazine–O_2 reaction to yield H_2O_2, followed by the formation of $OH^•$; $OH^•$ attacked 6-MP to produce disulfide radical anion ($RSSR^{•−}$), which reacted with the dissolved oxygen (O_2) to yield superoxide radical anion ($O_2{}^{•−}$); the further reaction of $O_2{}^{•−}$ with lucigenin led to light emission. This work discovered a new nanoparticle-involved CL reaction, revealed the effect regulation of the compounds containing hydroxyl, carboxyl, carbonyl, amino, and sulfur groups on the CL reaction. Since the CL enhancement by thiol-containing compounds such as Hcy, GSH, Cys and 6-MP of the lucigenin–hydrazine–Pt NPs system are very strong, it is possible to develop HPLC method combined with the present CL detection system for simultaneous determination of such thiol-containing compounds. Further work is under investigation.

Acknowledgements

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