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A novel selenium nanoparticles-enhanced chemiluminescence system for determination of dinitrobutylphenol

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ABSTRACT

A novel selenium nanoparticles (Se NPs)-amplified chemiluminescence (CL) reaction, Se NPs–potassium permanganate–dinitrobutylphenol (DNBP), for the determination of DNBP at gram per milliliter level is described. In the present study, it was found that direct reaction of DNBP with potassium permanganate ($KMnO_4$) in the acidic mediums elicited light emission, which was greatly enhanced by selenium nanoparticles. Under optimum conditions, the CL intensity is linearly related to the concentration of DNBP in the range of 1.0×10^{-7}–8.0×10^{-5} g mL^{-1} with a detection limit (3σ) of 3.1×10^{-8} g mL^{-1}. The relative standard deviation for 11 determinations of 2.5×10^{-5} g mL^{-1} DNBP is 2.07%. The Se NPs were prepared by the chemical hydrothermal method. It was found that catalytic properties of Se NPs were higher than those of microparticles (MPs). In addition, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the Se NPs. Appropriate sensitivity, selectivity and precision were among notable features of the proposed method. The method was successfully applied to the determination of DNBP in the water samples of different origins. Moreover, the possible mechanism for the new CL reaction was also discussed.

1. Introduction

Environmental pollution by toxic alkyl dinitrophenolic compounds can be detrimental to human health and the environment [1]. DNBP is a typical example of this class of toxic compounds [2]. It is usually used as a polymerization inhibitor for the production of styrene in petrochemical industries and also as a pesticide in agriculture industries [3]. Irregular release of DNBP containing wastewater to environment can be detrimental due to its high toxicity and carcinogenicity to mammals, fish and other aquatic organisms [2,4]. Hence, the determination of DNBP is very important for evaluating the total toxicity of environmental samples. A literature survey reveals several methods for DNBP determination including gas chromatography (GC), liquid chromatography (LC) and high-performance liquid chromatography (HPLC) [2–4]. On the other hand, CL methods due to their attracting features such as simplicity, simple and inexpensive instrumentation, high sensitivity and rapidity and low background signals, have received keen attention [5,6]. Hence, CL methods have become important and powerful analytical tools in various fields, such as biotechnology, food analysis, environmental analysis, pharmaceutical analysis and clinical tests [5,7–9]. They usually involve the oxidation of a suitable substrate (or analyte) to produce an excited species, which then emits light upon relaxation to ground state. Although many CL reagents have been investigated, only a few number of CL systems have been widely used in analytical chemistry [6,10–13]. Among them, $KMnO_4$ in acidic medium has got greater development recently, perhaps, because the reagent is cheap and easily available [7,14–16]. In some of CL-based methods, the CL emission generated during oxidation of organic molecules is of relatively low intensity due to low quantum yield [13,17]. Therefore, enhancement of CL emission for the aim of higher sensitivity is essential for analytical applications. To this aim, in recent years, nanomaterials including metal and semiconductor nanoparticles with unique physical and chemical properties, can participate in CL reactions as reductants, catalysts, luminophors and nano-sized reaction platforms to catalyze redox CL reactions, providing enhanced CL emission [18,19]. For example, it has been demonstrated that, nanoparticles of metals, such as silver [20], gold [13,21–23], platinum [24], as well as semiconductors, such as CdTe [25,26], CdSe/CdS [27] and TiO_2 [17] have been used as signal enhancers. However, to the best of authors' knowledge, Se nanoparticles have not been so far reported as an enhancer in CL systems.

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In the present paper, we have proposed for the first time a novel CL method for determination of DNBP. In this context, Se NPs were synthesized by the chemical hydrothermal method and then its effect to the new $KMnO_4$–DNBP CL system was explored. Moreover, it was found that Se NPs could act as a nanocatalyst on the $KMnO_4$–DNBP CL reaction in acidic solution to produce a relatively intense CL emission. Therefore, under the optimized conditions, the novel selenium nanoparticles-enhanced CL system was applied to the determination of DNBP in water samples.

2. Experimental

2.1. Reagents and materials

All the reagents were of analytical grade, and were used without further purification. The stock standard solution (5.0×10^{-4} g mL^{-1}) of DNBP (Petrochemical Co. Tabriz, Iran) was prepared by dissolving DNBP in slightly basic water. Double distilled water was used throughout. The test standard solutions were freshly prepared by appropriate dilution of the stock standard solution with water when used. $KMnO_4$ (Merck Co. Germany) stock solution (8.0×10^{-2} mol L^{-1}) was prepared in a brown bottle and kept in a dark room. Sodium selenite, hydrazine chloride, hydrochloric acid, sulfuric acid, nitric acid and phosphorous acid were purchased from Merck Co. (Germany). Cation-exchanging resin (Fluorosulfonic acid Nafion SAC-13, granules) was purchased from sigma Aldrich Co. (Germany).

2.2. Apparatus

The CL signals were monitored by FB12 luminometer (Berthold Detection Systems, Germany). Ultraviolet–visible (UV–vis) spectra were monitored by UV–vis spectrophotometer (WPA lightwave S2000, England) in the range of 200–800 nm. The morphology of materials was examined by a scanning electron microscope SEM (Hitachi S-4200, Japan). To determine the crystal phase composition and average crystalline size of synthesized Se NPs sample, XRD measurements were carried out at room temperature by using Siemens X-ray diffraction D5000 (California, USA), with Cu Kα radiation. The accelerating voltage of 40 kV and emission current of 30 mA were used. The average crystalline size of the samples was calculated according to Debye–Scherrer formula [28].

2.3. Procedure

CL detection was carried out in a 3 mL test tube in the sample holder of the luminometer. A 1 mL portion of solution containing $KMnO_4$ (8.0×10^{-4} mol L^{-1}) and a 1 mL portion of solution containing HCl (0.5 mol L^{-1}) were added into the cell. Then a 1 mL portion of sample solution containing appropriate concentration of analyte and Se NPs were added into test tube to initiate the CL reaction. The progress of the reaction was continuously monitored on a computer connected to the luminometer. Maximum CL intensity was used as analytical signal.

2.4. Sample treatment

Water samples from different sources, namely: irrigation, ground and river waters, were freshly collected in plastic flasks and immediately filtered with polyamide membrane filters of 0.45 μm to remove the suspended solid matter and stored in glass flasks protected from light at 4 °C in the refrigerator. They were used within 1 week. Prior to analysis, 10 mL water samples were spiked with 0.25, 0.5, 1.5, 2, 2.5 and 3 mL DNBP standard solutions (5.0×10^{-4} g mL^{-1}) and diluted to 25 mL with double distilled water, in order to obtain solutions containing 0.50, 1.00, 3.00, 4.00, 5.00 and 6.00×10^{-5} g mL^{-1}, respectively. Then, these solutions were passed through the ion exchanger III packed column with flow rate of 4 mL min^{-1}. The amount of DNBP in the collected solution was determined according to the general procedure and using standard addition method.

2.5. Synthesis of Se NPs and Se MPs

Se NPs were synthesized by the hydrothermal method as follows: sodium selenite (1 mmol) and hydrazine chloride (2 mmol) were added to distilled water (60 mL), and stirred well for 10 min at room temperature. Afterward, the mixture was transferred to a 100 mL Teflonlined autoclave. The autoclave was sealed, maintained at 150 °C for 24 h, and then cooled to room temperature. The optimum conditions for this reaction are pH = 3, temperature 150 °C and reaction time 24 h. The obtained black precipitate was filtered and washed with ethanol and water. It was dried at room temperature. Yields for the products were 90–95%. At basic media, the Se disproportionate to Se^{2-} and SeO_4^{2-}, then this reaction occurs at acidic pH. The overall chemical reaction of the synthesized Se NPs was presented in the following equation: (1).

$$Na_2SeO_3 + 2N_2H_4 \cdot HCl \xrightarrow{150\ ^{\circ}C\ \text{for}} Se + 2N_2 + 2H_2 + 3H_2O + 2Na^{+}Cl^{-} \quad (1)$$

Se microparticles (MPs) were synthesized as follows: sodium selenite (1 mmol) and hydrazine chloride (2 mmol) were added to distilled water (60 mL), and stirred well for 10 min at room temperature. Afterward, the mixture was maintained at 150 °C for 24 h, and then cooled to room temperature. The optimum conditions for this reaction are pH = 10, temperature 150 °C and reaction time 24 h. The obtained precipitate was filtered and washed with ethanol and H_2O_2. It was dried at room temperature. Yields for the products were 90–95%. At basic media, the Se disproportionate to Se^{2-}, so further oxidation with H_2O_2 leads to the production of Se MPs.

3. Results and discussion

3.1. XRD spectrum and SEM image of Se NPs

The formation of Se NPs can easily be confirmed by XRD spectrum (Fig. 1a). It can be observed from Fig. 1a that the peaks in XRD are at $2\theta = 23^{\circ}, 28^{\circ}, 42^{\circ}, 46^{\circ}$ and 52° which corresponded to Se NPs of tridimensional phase. The average crystalline size of the samples was 15 nm according to Debye–Scherrer formula [28].

The SEM images of the synthesized Se NPs and Se MPs are shown in Fig. 1b and c. It shows that the prepared nanoparticles and microparticles are spherical in shape and the size ranges from 15 nm to 30 nm and 0.1–0.5 μm, respectively. The conclusion drawn from XRD and SEM studies of Se NPs are in corroboration with each other. Thus, the present method is capable of producing spherical Se NPs.

3.2. CL reaction enhanced by Se NPs

Preliminary studies indicated that upon oxidation of DNBP by $KMnO_4$ acidic medium, CL occurred and emission intensity was dependent on DNBP concentration. Moreover, we have found that in the presence of Se NPs in the DNBP solution, a significant enhancement in CL intensity can be observed. The CL intensity–time response curves are shown in Fig. 2. In order to confirm the enhancing role of Se NPs, blank experiments were carried out

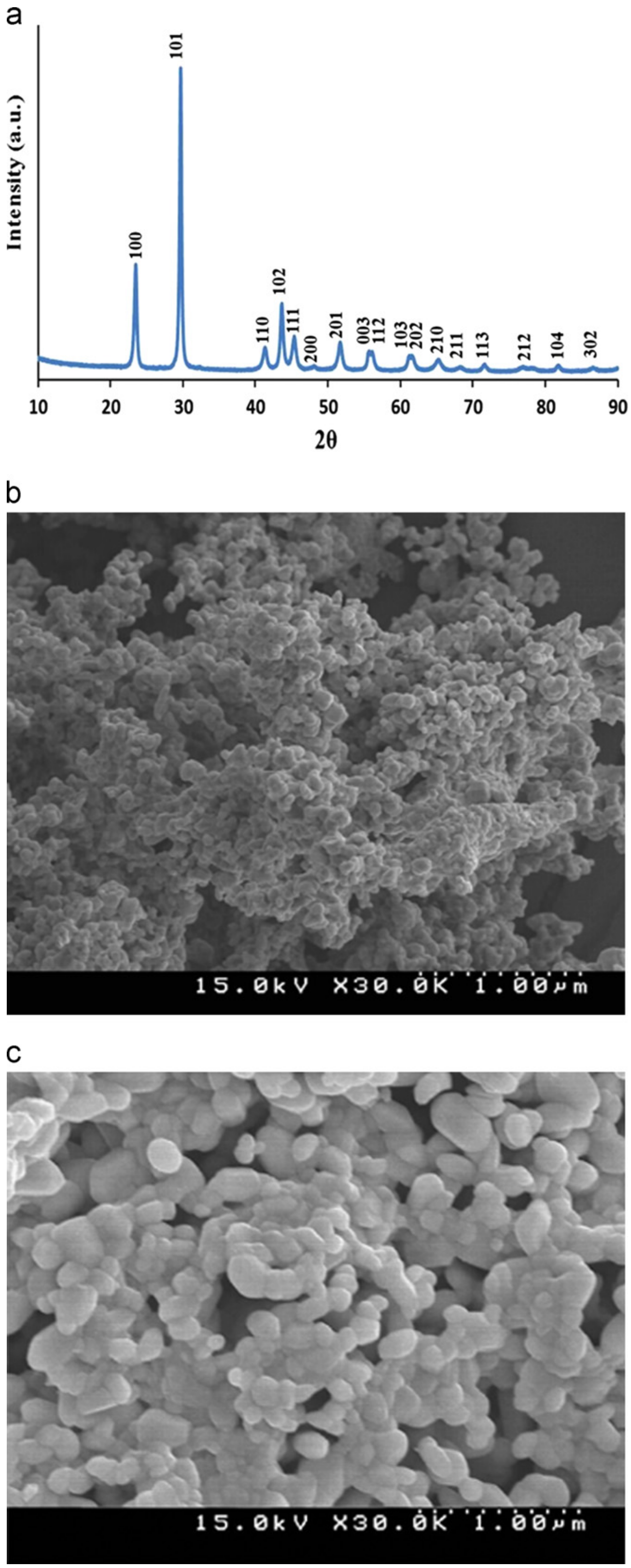

Fig. 1. (a) XRD pattern of the synthesized Se NPs; (b) SEM image of synthesized Se NPs and (c) SEM image of synthesized Se MPs.

using sodium selenite and hydrazine chloride solutions in concentrations used for the preparation of NPs. No enhancing effect was observed. Also, we examined Se MPs effect in $KMnO_4+DNBP$ CL system (Fig. 2). No significant enhancing effect was observed.

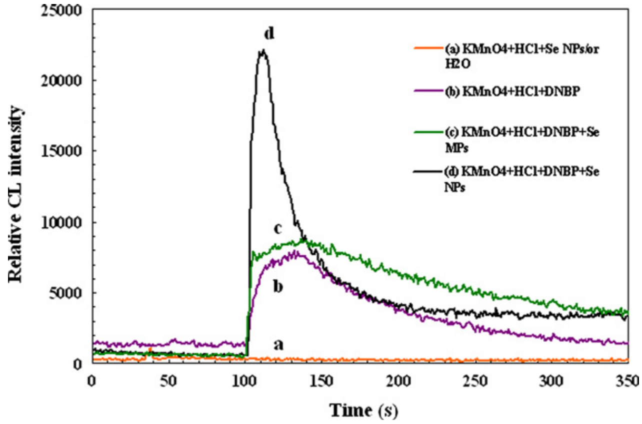

Fig. 2. Kinetic curves for $KMnO_4+DNBP+Se$ NPs/MPs CL systems. Conditions: the concentrations of $KMnO_4$, HCl, DNBP, Se MPs and Se NPs were 8×10^{-4} mol L^{-1}, 0.5 mol L^{-1}, 2.5×10^{-5} g mL^{-1}, 1000 mg L^{-1} and 1000 mg L^{-1}, respectively.

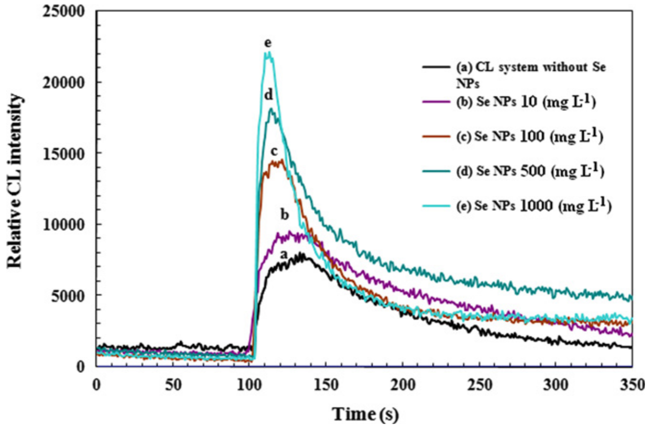

Fig. 3. Kinetic curves for $KMnO_4+DNBP+Se$ NPs CL system in the presence of various Se NPs concentrations. Conditions: the concentrations of $KMnO_4$, HCl and DNBP were 8×10^{-4} mol L^{-1}, 0.5 mol L^{-1} and 2.5×10^{-5} g mL^{-1}, respectively.

These observations confirm that the catalytic effect is due to the Se NPs. So, we examined Se NPs with various concentrations in $KMnO_4+DNBP$ CL system (Fig. 3). It can be seen that the CL signals increase with an increase in the concentration of Se NPs. The kinetic curves of CL reaction in the absence and presence of Se NPs (Fig. 2) have shown that the CL intensity reached a maximum value in 40 and 10 s after injection of DNBP and mixture of DNBP and Se NPs solutions, respectively. It should be noted that here in the acidic $KMnO_4$–DNBP CL system is a slow CL reaction, but in the presence of Se NPs the acidic Se NPs–$KMnO_4$–DNBP CL system is a relatively rapid CL reaction. Therefore, the effect of Se NPs is so appreciable in terms of time evolution of CL. Close examination of Fig. 3 has revealed that the maximum CL signal in the case of Se NPs catalyzed reaction achieved at around 10 s while in the absence of the catalyst the maximum reached at around 40 s. Moreover, when concentrations of Se NPs were significantly increased up to 1000 mg L^{-1}, the difference between the rates of non-catalyzed and catalyzed reactions became more considerable.

3.3. Optimization of operational conditions

Permanganate CL emission intensity is critically dependent on the type and concentration of acid [7,15]. Therefore, with a view to investigate the effects of different acidic media on the CL system, several acids including hydrochloric acid, sulfuric acid, nitric acid and phosphorous acid with different concentrations were examined. The results revealed that the highest CL signals were obtained in hydrochloric acid (Fig. 4a) [21]. The influence of hydrochloric acid concentration on the CL intensity was investigated at different concentrations in the range of 0.1–4 mol L^{-1} (Fig. 4b). The maximum CL intensity was obtained at 0.5 mol L^{-1} hydrochloric acid. Therefore, 0.5 mol L^{-1} hydrochloric acid was chosen for the subsequent experiment.

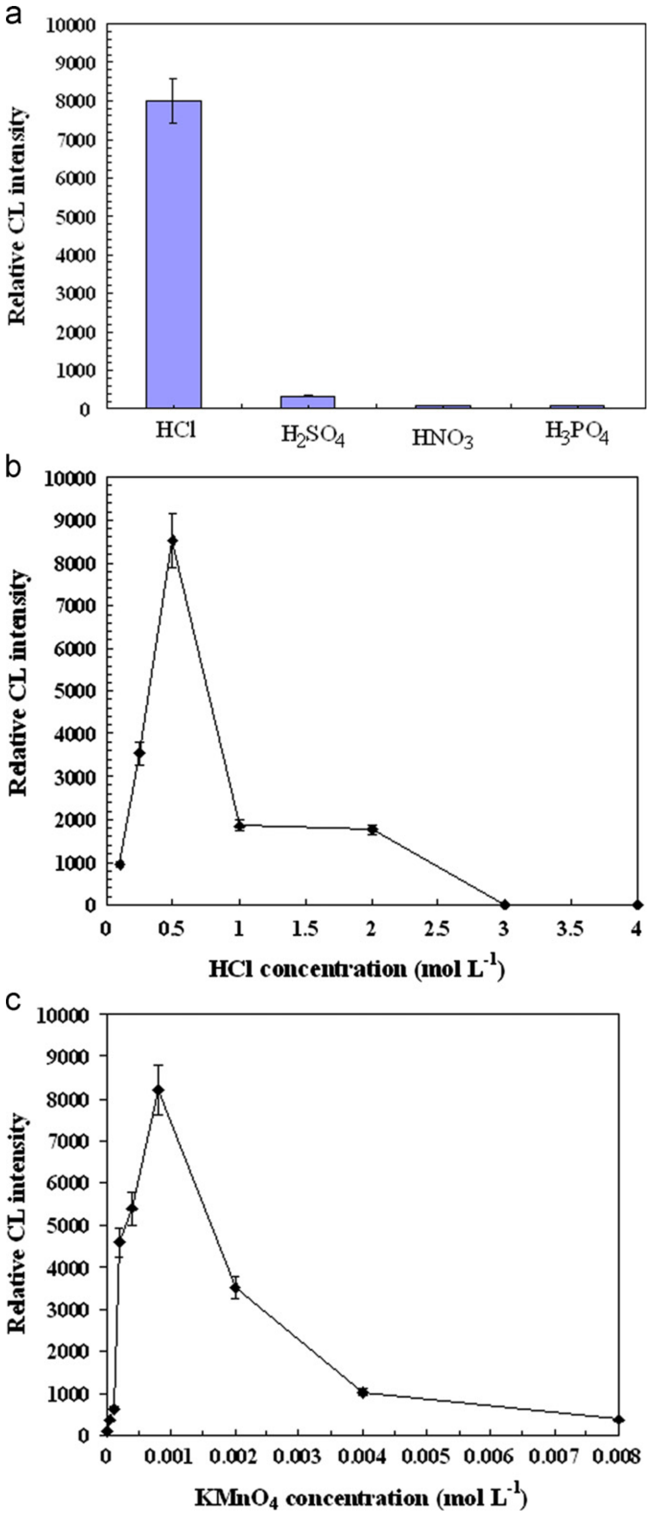

Fig. 4. Optimization of the CL operational conditions: (a) effect of different kinds of acids. Conditions: the concentrations of $KMnO_4$, HCl, H_2SO_4, HNO_3, H_3PO_4 and DNBP were 8×10^{-4} mol L^{-1}, 0.5 mol L^{-1}, 0.5 mol L^{-1}, 0.5 mol L^{-1}, 0.5 mol L^{-1} and 2.5×10^{-5} g mL^{-1} respectively; (b) effect of concentration of hydrochloric acid. Conditions: the concentrations of $KMnO_4$ and DNBP were 8×10^{-4} mo L^{-1} and 2.5×10^{-5} g mL^{-1} respectively and (c) effect of concentration of $KMnO_4$. Conditions: the concentrations of HCl and DNBP were 0.5 mol L^{-1} and 2.5×10^{-5} g mL^{-1} respectively.

The effect of $KMnO_4$ concentration on the CL intensity was examined in the range of 1×10^{-5}–8×10^{-3} mol L^{-1}. The results showed that the CL intensity increased with the concentration of $KMnO_4$ to 8×10^{-4} mol L^{-1}, thereafter, the CL intensity decreased (Fig. 4c) may be due to self-absorption phenomenon [14,29]. Therefore, 8×10^{-4} mol L^{-1} $KMnO_4$ was taken as a optimum value. With a view to acquire the highest CL intensity in hope for obtaining the maximum possible sensitivity of the system, the effect of concentration of Se NPs was investigated in the range of 10–2000 mg L^{-1}. As shown in Fig. 3, the CL intensity increased with increasing the concentration of Se NPs and reached a maximum CL emission at 1000 mg L^{-1} of Se NPs. At concentrations higher than 1000 mg L^{-1} the CL intensity decreased. For simplifying Fig. 3 the decrease of CL intensity at Se NPs of higher than 1000 mg L^{-1} was not shown in Fig. 3. This phenomenon may arise in the following possible ways:

When the concentration of Se NPs was too high, the interactions among particles were strong and the CL energy was transferred among particles which were in small distance [18].

Turbidity of solution in high Se NPs concentrations may also be involved in this phenomenon.

3.4. Analytical parameters

Under optimum conditions, linear calibration ranges were obtained for DNBP and detection limit (LOD) was calculated. The characteristic parameters for the calibration ranges and detection limit of the determination of DNBP are listed in Table 1. In addition, the experiment results obtained from our proposed method were compared with the analytical methods published in literature, previously (see Table 2). The comparison results showed that the determination of DNBP was made mainly with chromatographic methods such gas chromatography [30], liquid chromatography coupled with mass spectrometry [31] and high pressure chromatography [32]. However, these techniques have their respective advantages: suffer from some shortcomings such as high commercial price, long and laborious procedure, need for well skilled people and sometimes need for derivation, pre-concentration and extraction steps that increase the risk of sample loss and will not lead to determination of sample [31,32]. Furthermore, electrochemical methods have also been used for determination of DNBP in environmental samples. As an example Sreedhar et al. [34] have applied differential pulse adsorptive stripping voltammetric at a modified electrode for DNBP determination with the detection limit of 1.0×10^{-10} mol L^{-1} (see Table 2). It should be stated that in comparison with most of the methods used for determination of DNBP (Table 2), the proposed simple and rapid method in the present work provided acceptable and somehow better analytical figures of merit with relatively cheap apparatus. Besides these, the reagents are stable and inexpensive.

3.5. Interference

The influence of some materials such as some inorganic ions and phenol often found in water samples were investigated on the determination of DNBP by the developed CL method. Analyses were carried out for a fixed concentration of DNBP (2.5×10^{-5} g mL^{-1}) with increasing amounts of these species. The tolerable limit of a foreign species was taken if it caused a relative error of less than 5% and the result was shown in Table 3. As it is clear from the results,

Table 1
Calibration ranges and analytical features for determination of DNBP.

Linear range (g mL^{-1})	Linear equation	Correlation coefficient (*R*)	Detection limits (g mL^{-1})	RSD (%)
1×10^{-7}–1×10^{-6}	$\Delta I^{a} = 6E{+}09\ C^{b} + 1260.8$	0.9902	3.1×10^{-8}	2.07
1×10^{-6}–8.0×10^{-5}	$\Delta I^{a} = 5E{+}08\ C^{b} + 6921.2$	0.9978		

[a] The relative CL intensity (the difference between CL intensity in the absence (I_0) and presence of DNBP (I)).
[b] Concentration of DNBP (g mL^{-1}).

Table 2
Comparison of the present work with some established methods for the determination of DNBP.

Analytical method	Linear range (g mL^{-1})	Detection limit (g mL^{-1})	Reference
Electrochemical method (voltammetric sensors)[a]	1.92×10^{-6}–2.4×10^{-5}	5.47×10^{-7}	[36]
Differential pulse adsorptive stripping voltammetric[b]	4.8×10^{-11}–7.2×10^{-8}	2.4×10^{-11}	[35]
Gas chromatography using an electron-capture detector	0.1×10^{-9}–5.0×10^{-9}	0.04×10^{-9}	[31]
High pressure 1iquid chromatography	5.0×10^{-9}–45×10^{-9}	0.6×10^{-9}	[37]
Liquid chromatography/atmospheric pressure chemical ionization mass spectrometry[c]	50×10^{-6}–250×10^{-6}	50×10^{-9}	[32]
On-line liquid chromatographic precolumn-based column switching techniques[d]	1.0×10^{-9}–25×10^{-9}	0.5×10^{-9}	[38]
Hollow fiber supported liquid membrane extraction and high performance liquid chromatography	25×10^{-12}–2.0×10^{-10}	8.0×10^{-12}	[33]
Preconcentration using quinolin-8-ol and high pressure 1iquid chromatography	0.1×10^{-6}–30×10^{-6}	60×10^{-9}	[39]
Liquid chromatography	0.1×10^{-9}–7.0×10^{-9}	0.1×10^{-9}	[40]
The proposed CL method in this work	1.0×10^{-7}–8.0×10^{-5}	3.1×10^{-8}	–

[a] An electrochemical method in which the electrode surface is modified with an appropriate material to produce a voltammetric sensor.
[b] A modern electroanalytical method which allows for the accumulation of analytes on the electrodes through a non-electrolytic process for trace determination of analytes.
[c] A multiresidue analytical method for determining thermolabile and polar pesticides in water samples.
[d] A method in which a pre-column procedure with a valve switching procedure can be used to select a particular column to separate a particular sample.

Table 3
Tolerance limit of various coexistent substances on the determination of 2.5×10^{-5} (g mL^{-1}) DNBP.

Interferences	Tolerance ratio (species: DNBP)
K^{+}, Na^{+}, SO_4^{2-}, Cl^{-}	1000
Al^{3+}, NO_3^{-}, PO_4^{3-}, CO_3^{2-}	500
Mg^{2+}, Ca^{2+}	50
Fe^{3+}	10
Cu^{2+}, Zn^{2+}, Mn^{2+}, phenol	1
Mg^{2+}, Ca^{2+}	500[a]
Mn^{2+}	250[a]

[a] After passing water containing DNBP through cation-exchanging resin column.

Table 4
Results for the determination of DNBP in real water samples with different amounts of DNBP.

Samples	Added (g mL^{-1})	Proposed method (g mL^{-1}, $n=5$)		
		Found[b] (g mL^{-1})	Recovery (%)	*t*-Statistic[c]
Water samples	0	ND[a]	–	–
Irrigation water sample	5.00×10^{-6}	$0.480 \pm 0.10 \times 10^{-6}$	97.38 ± 4.2	0.99
	1.00×10^{-5}	$0.974 \pm 0.14 \times 10^{-5}$	97.40 ± 3.8	1.90
Ground water sample	3.00×10^{-5}	$2.880 \pm 0.15 \times 10^{-5}$	96.16 ± 2.2	2.05
	4.00×10^{-5}	$3.932 \pm 0.16 \times 10^{-5}$	98.25 ± 1.1	2.90
River water sample	5.00×10^{-5}	$4.921 \pm 0.12 \times 10^{-5}$	98.45 ± 3.2	2.29
	6.00×10^{-5}	$5.810 \pm 0.16 \times 10^{-5}$	97.85 ± 2.5	3.46

[a] Not detected.
[b] Mean of five determinations ± standard deviation.
[c] *t*-Critical $= 4.30$ for $n=5$ and $P=0.05$.

some cations interfere with the CL reaction. Passing the sample solution through a cation exchanger column can solve this problem. For instance, according to our results, even 500-fold Mg^{2+} and Ca^{2+} and 250-fold Mn^{2+} does not interfere with DNBP determination after passing the solutions of real water samples containing interfering cations and DNBP (see Table 3) from a cation exchanger column. Based on these results, we conclude that the CL method provides selective determination of DNBP in water samples.

3.6. Determination of DNBP in real water samples

The procedure was easily applied to the determination of DNBP in real water samples. However a preliminary step for elimination of some interfering cations was found to be necessary. Cation-exchanging resin (Nafion) was used for this purpose as a common cation exchanger. In order to validate the method, known quantities of DNBP were added into the real water samples, the samples were prepared and analyzed according to the general procedure described in section 2. All the above experiment results are detailed in Table 4. Statistical analysis of these results using Student *t*-test showed that there are no significant differences between added and found values [35].

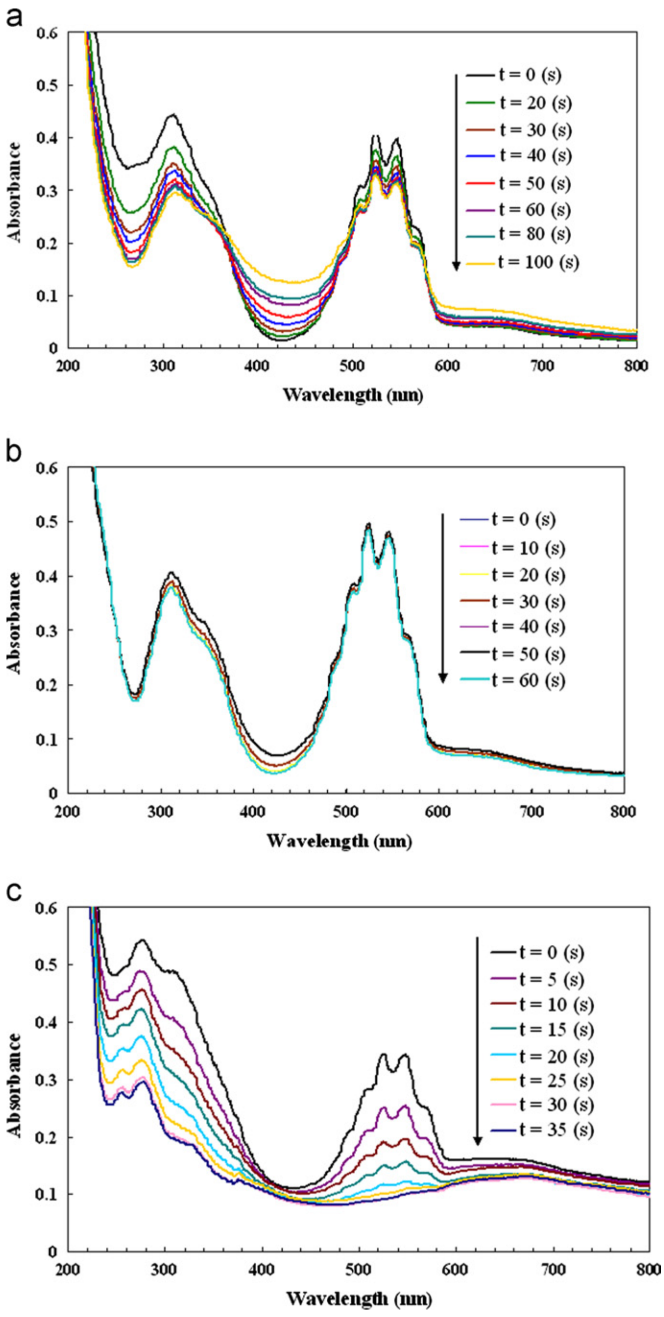

Fig. 5. (a) UV–vis absorption spectra for $KMnO_4$+DNBP CL system during 100 s; (b) UV–vis absorption spectra for $KMnO_4$+Se NPs system during 60 s; (c) UV–vis absorption spectra of $KMnO_4$+DNBP+Se NPs CL system during 35 s. Conditions: the concentrations of $KMnO_4$, HCl, DNBP and Se NPs were 8×10^{-4} mol L^{-1}, 0.5 mol L^{-1}, 2.5×10^{-5} g mL^{-1} and 1000 mg L^{-1}, respectively.

3.7. Possible CL mechanisms

Although various emitting species have been proposed for acidic $KMnO_4$ CL reactions, recently it has been well confirmed that red CL emission in these systems emanates from relaxation of Mn(II) excited state to the ground state [21,36,37]. Indeed, it has been reported that the oxidation of a substrate by Mn(VII) generates Mn(III) and possibly a transient species, which then reacts with Mn(III) in solution to produce Mn(II)* excited state [29]. In order to elucidate the possible mechanism, UV–vis absorption spectra (Fig. 5) in addition to CL intensity–time curve (Fig. 2) were recorded for the CL system in the presence and absence of Se NPs.

The CL intensity–time curve of $KMnO_4$–DNBP system (Fig. 2a) shows that the DNBP reacts slowly with $KMnO_4$ to produce a relatively weak CL emission. In addition, the low rate of redox reaction can be verified by the UV–vis absorption spectra of this system (Fig. 5a), since the two UV–vis absorption peaks of $KMnO_4$ reduced slowly during 1 min of recording spectra.

In order to study the role of Se NPs on the CL system, following experiments were made. The UV–vis absorption spectra and the CL intensity–time curve of $KMnO_4$–Se NPs system were recorded (Fig. 5b). Based on obtained spectra, it can be concluded that no chemical reaction occur between Se NPs and $KMnO_4$. As can be seen from Fig. 2a and b the CL of Se NPs–$KMnO_4$–DNBP system is more intense than that of the $KMnO_4$–DNBP system. Moreover, the two UV–vis absorption peaks of $KMnO_4$ in the Se NPs–$KMnO_4$–DNBP system are lower than that of obtained in the $KMnO_4$–DNBP system (Fig. 5c and a). Therefore, it might be suggested that Se NPs fasten the electron transfer and consequently, redox reaction of $KMnO_4$–DNBP and accelerate Mn(III) and Mn(II)* generation, leading to higher CL intensity. Based on the above experimental results and the other studies, the possible mechanism of CL reaction may be attributed to the following reactions in its simplest form in the presence of Se NPs may be presented as follows:

$$\mathrm{MnO_4^- + 4DNBP + 4H^+ \xrightarrow{Surface\ of\ Se\ NPs} 4DNBP_{ox} + Mn(III)} \quad (2)$$

$$\mathrm{2Mn(III) + DNBP \xrightarrow{Surface\ of\ Se\ NPs} DNBP_{ox} + 2Mn(II)^* + 2H^+} \quad (3)$$

$$\mathrm{Mn(II)^* \rightarrow Mn(II) +} h\upsilon \quad (4)$$

4. Conclusions

The Se NPs enhanced-CL method proposed here is simple and showed improved selectivity. Furthermore, it gives sufficient sensitivity without using an expensive CL reagent. The method has been successfully applied to the analysis of DNBP in water samples of different origins and the results were in reasonable agreement with a reference method.

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