



Organo-modified layered double hydroxide-catalyzed Fenton-like ultra-weak chemiluminescence for specific sensing of vitamin B₁₂ in egg yolks

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ABSTRACT

In general, the chemiluminescence (CL) sensing of vitamin B₁₂ is achieved by determining Co(II) liberated from acidified vitamin B₁₂ by a luminol system. However, the luminol system for sensing vitamin B₁₂ has poor selectivity due to serious interference from other metal ions. In this study, as a novel CL amplifier of the Co(II)+H₂O₂+OH⁻ ultra-weak CL reaction (Fenton-like system), dodecylbenzene sulfonate (DBS)-layered double hydroxides (LDHs) have been applied to the specific determination of vitamin B₁₂ by liberating Co(II). The CL intensity increased with increasing the concentration of vitamin B₁₂ in a wide range from 1.0 ng mL⁻¹ to 5 μg mL⁻¹ with a detection limit of 0.57 ng mL⁻¹ (S/N=3). The proposed method has been successfully applied to determine vitamin B₁₂ in egg yolk with simple procedures, shorter time and higher selectivity. Recoveries from spiked real samples were 96–103%. The results of the proposed method for sensing vitamin B₁₂ in real samples were agreed with those obtained by the standard inductively coupled plasma mass spectrometry (ICP-MS) method. To the best of our knowledge, this is the first report on the CL sensing of vitamin B₁₂ with high selectivity in the absence of luminol.

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1. Introduction

Vitamin B₁₂ is an essential nutrient linked to human growth and cell development [1]. The daily requirement of vitamin B₁₂ is relatively low in comparison to other vitamins, and thus exposure to excessive amounts of vitamin B₁₂ can induce asthma and folic acid deficiency [2]. On the other hand, its deficiency is associated with a variety of disorders and human diseases, such as weakness, fatigue, renal dysfunction, diabetes, pernicious anemia and nerve degeneration [3]. It is well known that vitamin B₁₂ must be obtained through diet because it cannot be synthesized in the human body [4]. Acting as a nutrient-dense food, eggs contain a substantial amount of various essential vitamins, and thus they are considered as an important source of vitamin B₁₂, in which vitamin B₁₂ is mainly found in egg yolks [5]. As a result, the accurate measurement of vitamin B₁₂ in egg yolks is desirable for research purposes and routine clinical use.

The classical analytical techniques for quantifying vitamin B₁₂ currently include microbiological [6], spectrophotometric [7],

fluorescent [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], and electrochemical methods [10]. Nowadays, a chemiluminescence (CL) technique for the determination of vitamin B₁₂ is becoming a promising technique with reliability, fast response, cheap instrument, simple operation and high sensitivity [11–15]. Generally, the quantification of vitamin B₁₂ could be achieved by determining Co(II) liberated from acidified vitamin B₁₂ using the luminol CL system. However, these CL methods suffered from the low selectivity due to serious interference from other metal ions. Therefore, it is highly desired to employ the other CL systems in the absence of luminol for improving the CL selectivity towards vitamin B₁₂. To the best of our knowledge, the specific and precise CL measurements of vitamin B₁₂ are not available except for the luminol system at present. As a result, it is still an active field as well as a great challenge to attain this goal.

Layered double hydroxides (LDHs) are an important class of host-guest layered nanomaterials consisting of positively charged metal hydroxide sheets with charge-balancing intercalated anions and water molecules [16,17]. LDHs exhibit a well-defined layered structure with relatively large surface area, high porosity, high layer charge density and interlayer anion mobility [18]. Therefore, LDHs have been extensively employed as catalysts, ion exchangers, and adsorbents [19–22]. Recently, we have found that the galleries

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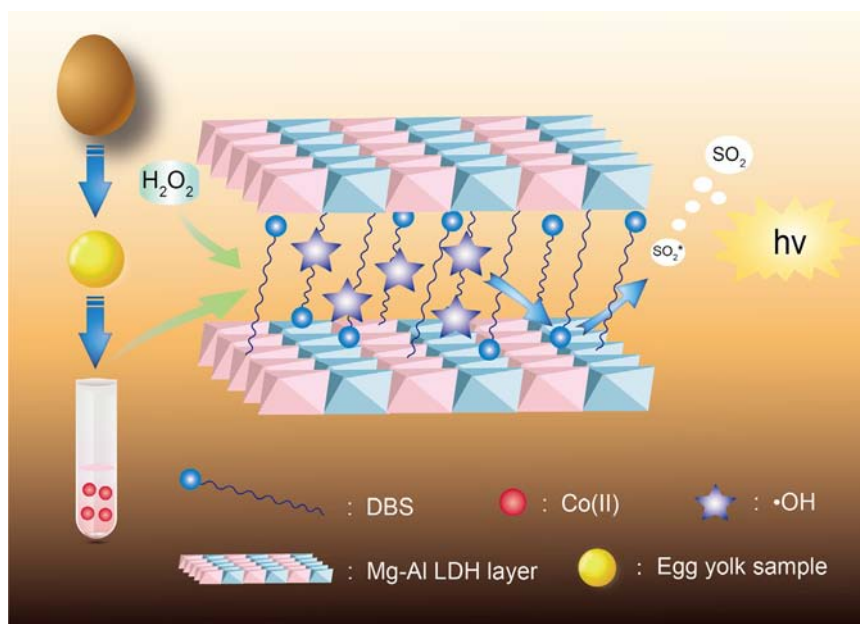


Fig. 1. Possible mechanism for the DBS-LDH-Co(II)+H₂O₂+OH⁻ system.

of the LDH could lead to the concentration of the CL reactants/intermediates on the surface or in the interlayer of the LDHs, facilitating the occurrence of the CL reactions [23,24]. It has been reported that the LDHs can enhance the CL signals of some ultra-weak CL systems, such as the IO₄⁻-H₂O₂ system, and peroxytrifluoromethane system [25–27]. Subsequently, the LDH-amplified ultra-weak CL emissions were successfully used for a wide variety of analytes in environmental and food samples [28–30].

Recently, we reported that organo-modified LDHs (*i.e.*, dodecylbenzene sulfonate DBS-modified LDHs) could significantly enhance an ultra-weak CL from Fenton-like reaction (Co(II)+H₂O₂+OH⁻) [31]. The DBS-modified LDH-induced CL enhancement of Fenton-like reaction was ascribed to the hydrophobic microenvironment of the intercalated DBS in LDHs, facilitating the formation of reaction intermediates. In this study, we tried to detect Co(II) liberated from acidified vitamin B₁₂ using the DBS-modified LDH-catalyzed Fenton-like CL system (Fig. 1). It was found that the CL intensity was proportional to the log concentration of vitamin B₁₂ in the range from 1.0 ng mL⁻¹ to 5 μg mL⁻¹, and the limit of detection (*S/N*=3) was found to be as low as 0.57 ng mL⁻¹. Therefore, a rapid, selective, sensitive and simple CL method to assay vitamin B₁₂ was successfully developed. Validation of the proposed method was checked by determining vitamin B₁₂ in egg yolks. To the best of our knowledge, here is the first example for CL sensing of vitamin B₁₂ with high selectivity in the absence of luminol.

2. Experimental

2.1. Reagents

Analytical grade chemicals including NaOH, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, HCl, HNO₃, H₂O₂, FeSO₄·7H₂O, FeCl₃, CuCl₂·2H₂O, MnSO₄·H₂O, Ni(NO₃)₂·6H₂O, Pb(NO₃)₂, CrCl₃·6H₂O, and ZnCl₂ were purchased from Beijing Chemical Reagent Company (Beijing, China). Uranine was purchased from Acros. Sodium dodecyl benzene sulfonate (SDBS) was purchased from Tokyo Chemical Industry Co. Ltd. Pure crystalline vitamin B₁₂ was purchased from Beijing HWRK Chem Co. Ltd. Working solutions of H₂O₂ were prepared daily from 30% (*v/v*) H₂O₂. A stock solution of vitamin B₁₂

(1.0 mg mL⁻¹) was prepared by dissolving 0.100 g of crystalline vitamin B₁₂ in 100 mL deionized water. All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (Milli Q, Millipore, Barnstead, CA, USA).

2.2. Apparatus

The powder X-ray diffraction (XRD) measurement was performed on a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu/Kα radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ angle of the diffractometer was stepped from 2° to 70° at a scan rate of 0.02°/s. The particle sizes and external morphology of the samples were observed on a transmission electron microscope (TEM, Tecnai G220, FEI Company). Scanning electron microscopy (SEM) was measured on a Hitachi (Japan) S-4700 field-emission scanning electron microscope. The fluorescence spectra were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at a scanning rate of 1500 nm/min. The excitation slit and the emission slit were maintained at 5.0 nm and 2.5 nm, respectively. The CL detection was conducted on an Ultra-Weak Luminescence Analyzer, which was purchased from institute of Biophysics, Chinese Academy of Science, Beijing, China (Biophysics Chemiluminescence, BPCL). An Agilent 7700 ICP-MS system (Agilent Technologies, Santa Clara, CA) was used to detect the Co(II) in egg yolks.

2.3. Synthesis of Mg-Al-NO₃ LDHs

The Mg-Al-NO₃ LDHs with different Mg/Al molar ratios were obtained by a co-precipitation method. The precipitation process was taken under low supersaturation conditions at constant pH. For Mg/Al molar ratio of 3, the salt solution (80 mL) containing Mg(NO₃)₂·6H₂O (0.06 mol) and Al(NO₃)₃·9H₂O (0.02 mol) was added dropwise to a 250 mL four-necked flask under vigorous stirring at room temperature, the pH value was adjusted to 10 with 2.0 M NaOH. The resulting white precipitate was continually stirred for 24 h at 65 °C. The whole reaction process was purged with N₂ throughout the experiment to avoid carbon dioxide uptake. The products were centrifugated, washed with degassed and deionized

water for three times, dried in vacuo at 65 °C for 24 h and ground to a fine powder.

2.4. Synthesis of Mg–Al–DBS LDHs

The typical anion exchange procedure was used to prepared Mg–Al–DBS LDHs. A 0.2 M SDBS aqueous solution (25 mL) was prepared by degassed and deionized water. A suspension of 1.0 g Mg–Al–NO₃ LDHs in the prepared SDBS solution was vigorously stirred at 80 °C for 24 h under nitrogen atmosphere. The as-prepared Mg–Al–DBS LDH suspension was stored at 4 °C for further use.

2.5. Acidification of standard vitamin B₁₂

It is important to acidify vitamin B₁₂ for the liberation of Co(II) using HNO₃ and HCl in order to further CL assay. Herein, vitamin B₁₂ was acidified according to the literature [14]. Briefly, 1.0 mg mL⁻¹ vitamin B₁₂ was acidified with 5.0 mL of 5.0 M HNO₃ by heating until the solution was evaporated completely, followed by adding 5.0 mL of 3.0 M HCl to remove the redundant HNO₃. The reaction mixture was further heated at 95 °C for 4 min and cooled at room temperature; the pH value of the obtained residue was adjusted to pH 7.0 with 5.0 M NaOH. The as-prepared solution was diluted with deionized water when required before the CL analysis.

2.6. Procedure for CL detection

The schematic diagram of the CL system was shown in Fig. S1. 200 μL 10 μg mL⁻¹ acidified vitamin B₁₂ solution was injected into the mixed solution containing 200 μL 100 mM Mg–Al–DBS LDH suspension and 100 μL 1.0 mM H₂O₂. The CL signals were monitored by a photomultiplier tube (PMT) adjacent to the CL quartz cell. The data integration time of the BPCL analyzer was set at 0.1 s per spectrum, and a work voltage of –1000 V was used for the CL detection. The CL signals were imported to the computer for data acquisition.

2.7. Sample pretreatment

Eggs from the supermarket in Beijing were pretreated according to the literature [13]. 5.0 g of boiled egg yolk was accurately weighed, and then it was ground and acidified ultrasonically with 50 mL of 0.5 M HCl until a homogeneous mixture was obtained. The obtained mixture was then centrifuged at 10,000 rpm for 10 min. The clear supernatant was filtered through a 0.45 μm filter and diluted as required prior to analysis. The as-prepared products were analyzed immediately by the proposed CL method and a standard ICP-MS method.

3. Results and discussion

3.1. Selective sensing towards Co(II) in Fenton-like-DBS–LDH CL system

The CL assays of Co(II) using luminol reaction system generally exhibit high sensitivity, but the detection selectivity towards Co(II) is relatively low [32,33]. Therefore, it is highly required to use sample pretreatments or separation techniques to improve the CL selectivity towards Co(II). In this study, the CL intensity of the DBS–LDH-amplified Fenton-like system of a series of metal ions was investigated in a static CL system established in Fig. S1. As shown in Fig. 2, an obvious increase in the CL intensity was observed upon the addition of 1.0 μM Co(II). However, little CL change occurred in the presence of common metal ions including Fe(III), Fe(II), Pb(II), Cu(II), Mn(II), Zn(II), Ni(II), Cr(III), and Al(III). Therefore, it is concluded that the present CL system is highly selective towards Co(II).

It has been reported that Cu(II) can also catalyze the decomposition of H₂O₂ in basic solutions to produce a weak CL emission (i.e., Cu(II)+H₂O₂+OH⁻ system) [34,35]. Accordingly, in order to clarify the mechanism of the striking CL selectivity towards Co(II), the kinetic CL intensity-time profiles for DBS–LDH–Co(II)+H₂O₂+OH⁻ system and DBS–LDH–Cu(II)+H₂O₂+OH⁻ system were almost the same (maximum at 0.3 s) except for the

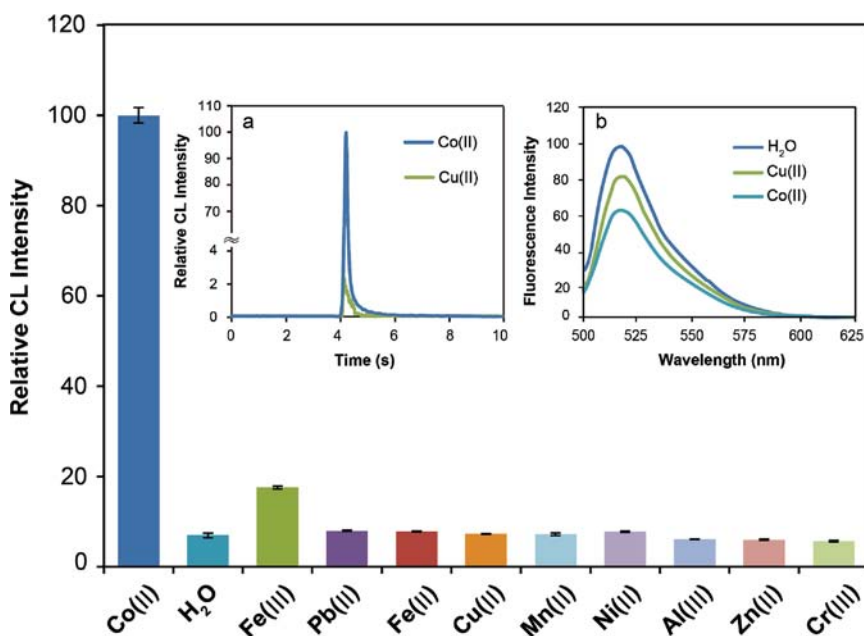


Fig. 2. Selectivity sensing of Co(II) over some common metal ions utilizing DBS–LDH-amplified Fenton-like CL reaction. Inset: (a) kinetic CL intensity-time profiles for the DBS–LDH–Co(II)+H₂O₂+OH⁻ system and DBS–LDH–Cu(II)+H₂O₂+OH⁻ system; (b) fluorescent spectra of uranine in the presence of the DBS–LDH–Co(II)+H₂O₂+OH⁻ system and DBS–LDH–Cu(II)+H₂O₂+OH⁻ system. The fluorescence excitation wavelength was set at 491 nm. The concentrations of each metal ion, uranine, H₂O₂ and DBS–LDH colloidal solution were 1.0 μM, 1.0 mM, 1.0 mM and 20 mg mL⁻¹, respectively.

differences of the CL intensities (see inset a of Fig. 2). These results indicated that the CL reaction rate of the DBS-LDH-Co(II)+H₂O₂+OH⁻ system was the same as that of the DBS-LDH-Cu(II)+H₂O₂+OH⁻ system; however, the amount of the intermediates generated during the CL reactions from the DBS-LDH-Co(II)+H₂O₂+OH⁻ system was much more than that from the DBS-LDH-Cu(II)+H₂O₂+OH⁻ system. On the other hand, the DBS-LDH-Co(II)+H₂O₂+OH⁻ system could lead to a greater decrease in the fluorescence intensity of uranine in comparison to the DBS-LDH-Cu(II)+H₂O₂+OH⁻ system (see inset b of Fig. 2), indicating the formation of the larger amount of hydroxyl radicals (•OH) in the presence of the DBS-LDH-Co(II)+H₂O₂+OH⁻ system [36].

3.2. Mg to Al molar ratios

In this study, the effect of Mg/Al molar ratios of Mg–Al DBS-LDHs between 2 and 4 on the CL intensity was investigated. The results showed that the CL intensity of the proposed system with Mg/Al molar ratio 3 was the strongest, and the higher and lower Mg/Al ratios resulted in a decrease of the CL intensity. The SEM image, TEM image and the representative XRD pattern of DBS-LDHs with a Mg/Al ratio of 3 indicated that the well-order layered structures with a high degree of crystallinity were formed (Fig. S2), facilitating the proceeding of the CL reaction. These results were almost in conformity with the literature [23].

3.3. Concentrations of H₂O₂ and DBS-LDH colloidal solution

The concentration of H₂O₂ was a key parameter for the DBS-LDH-Co(II)+H₂O₂+OH⁻ CL reaction. In this study, the effect of the concentration of H₂O₂ on the CL intensity was examined in the range of 0.5–10 mM (Fig. 3a). The results showed that the strongest CL intensity was observed at 1.0 mM H₂O₂, accompanying with the production of a small number of gaseous bubbles. The concentrations of H₂O₂ higher than 1.0 mM could induce a decrease in the CL intensity. Therefore, this system was operated at 1.0 mM H₂O₂ throughout this study.

On the other hand, the DBS-LDH colloidal solution can act as an efficient amplifier of the Co(II)+H₂O₂+OH⁻ CL reaction. Therefore, the concentration of DBS-LDHs played an important role in CL intensity. Note that the concentration of the as-prepared DBS-LDHs was calculated to be 56 mg mL⁻¹ by measuring the obtained solid content. As shown in Fig. 3b, the effect of the concentration of DBS-LDHs on the CL in the range of 5.0–56 mg mL⁻¹ was investigated. It was shown that the maximum intensity was obtained at a DBS-LDHs concentration of 20 mg mL⁻¹. When the concentrations of DBS-LDHs were higher than 20 mg mL⁻¹, the CL intensity increased slowly. In view of the consumption of the reagents, 20 mg mL⁻¹ was used as the optimal concentration of DBS-LDH colloidal solution.

3.4. Analytical performances

Under the optimum experimental conditions employed in this study, the CL intensity was proportional to the log concentration of vitamin B₁₂ in the range from 1.0 ng mL⁻¹ to 5 μg mL⁻¹ (Fig. 4). The regression equation was $\Delta I = 25.02 \log C + 4.2288$ ($R^2 = 0.997$), where ΔI was the relative CL intensity and C was the concentration of vitamin B₁₂, respectively. The detection limit for vitamin B₁₂ ($S/N=3$) was calculated to be 0.57 ng mL⁻¹ [13]. The relative standard deviation (RSD) for nine repeated measurements of 10 ng mL⁻¹ vitamin B₁₂ was 2.8%. Furthermore, the interference effects of various coexistent substances presented in egg yolk samples on the determination of vitamin B₁₂ were examined. A sample solution containing a fixed amount of vitamin B₁₂ (10 ng mL⁻¹) and different concentrations of each coexistent substance was analyzed by the proposed method. A coexistent substance was considered as non-interfering if the analytical CL signal variation was $\pm 5\%$ in comparison to the CL signal obtained in the absence of the coexistent substance. The results revealed that the proposed method showed very high selectivity towards vitamin B₁₂ (Table 1).

3.5. Real samples

In order to evaluate the applicability and reliability of the proposed methodology, it was applied for the determination of vitamin B₁₂ in egg yolk samples. The pretreated samples were diluted to an appropriate concentration with deionized water before analysis. To check the accuracy of the CL analysis, a standard ICP-MS method was used to measure the content of Co(II) liberated from acidified vitamin B₁₂ in egg yolk samples. The results in Table 2 indicate that vitamin B₁₂ can be detected in real sample and no obvious difference was observed between the proposed method and the standard ICP-MS method. These differences were statistically insignificant ($P > 0.05$) when the sample groups were used to undergo two-tailed unpaired *T*-tests [13]. The recoveries of vitamin B₁₂ obtained by the proposed method ranged from 96% to 103%. These results demonstrated that the present method could be efficiently used to determine vitamin B₁₂ in egg yolk samples.

4. Conclusions

In summary, the organo-modified LDHs were found to have a remarkable amplification of Fenton-like reaction of Co(II) CL reaction in basic solutions. The differences of the CL reaction kinetics and fluorescence intensity variation of uranine resulted from the DBS-LDH-Co(II)+H₂O₂+OH⁻ system and the DBS-LDH-Cu(II)+H₂O₂+OH⁻ system demonstrated that the larger amount

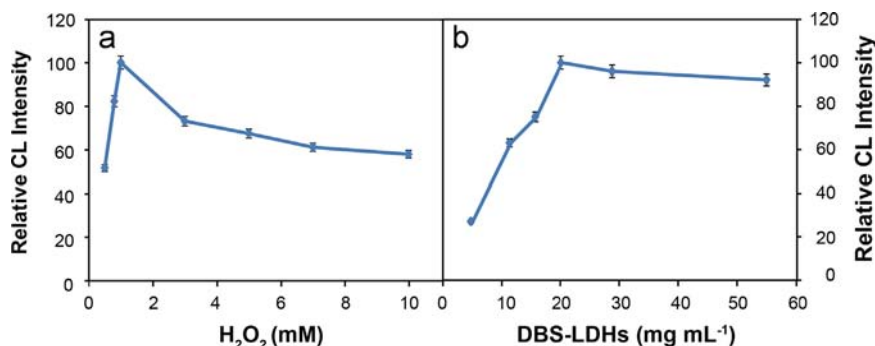


Fig. 3. Effects of various conditions on the DBS-LDH assembly-enhanced CL intensity: (a) concentration of H₂O₂ at 20 mg mL⁻¹ DBS-LDH colloidal solution; (b) concentration of DBS-LDH colloidal solution at 1.0 mM H₂O₂.

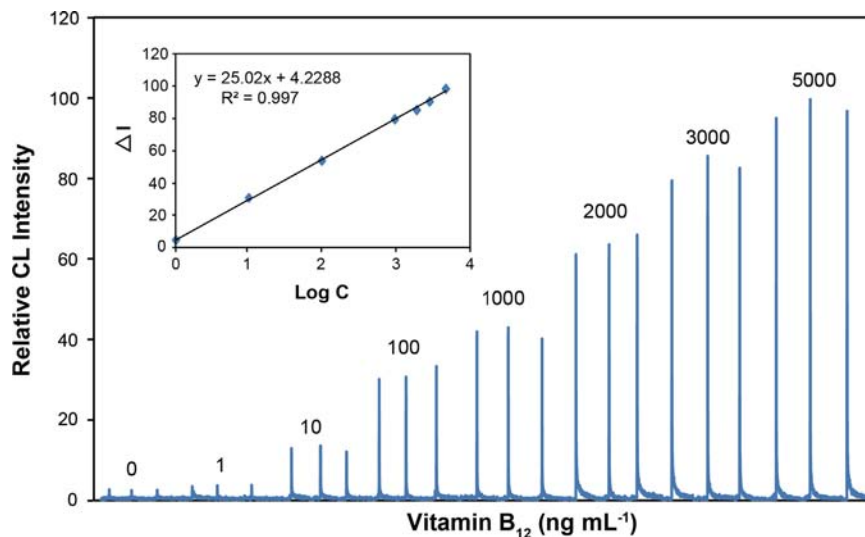


Fig. 4. CL intensity of the proposed system by adding different concentrations of vitamin B₁₂. Inset: the calibration curve for vitamin B₁₂. The concentrations of H₂O₂ and DBS-LDH colloidal solution were 1.0 mM and 20 mg mL⁻¹, respectively.

Table 1

Tolerance limit of various coexistent substances on the determination of 10.0 ng mL⁻¹ vitamin B₁₂.

Tolerance (ng mL ⁻¹)	Coexistent substances
1.0 × 10 ⁵	Na ⁺ , Mg ²⁺ , Al ³⁺ , NO ₃ ⁻ , F ⁻ , Cl ⁻ , Br ⁻ , SO ₄ ²⁻ , SO ₃ ²⁻ , CO ₃ ²⁻ , HCO ₃ ⁻ , glucose, sucrose
5.0 × 10 ⁴	Ca ²⁺ , Ag ⁺ , Fe ²⁺ , Sn ²⁺ , Sr ²⁺ , Zn ²⁺ , Ba ²⁺ , K ⁺ , Ac ⁻ , H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ , C ₂ O ₄ ²⁻
1.0 × 10 ⁴	Cu ²⁺ , Cr ³⁺ , Cd ²⁺ , Fe ³⁺ , Ni ²⁺ , Pb ²⁺ , Mn ²⁺

Table 2

Determination of vitamin B₁₂ in egg yolk samples.

Samples	CL method ^a (ng g ⁻¹)	ICP-MS method ^a (ng g ⁻¹)	Added (ng g ⁻¹)	Found ^a (ng g ⁻¹)	Recovery (%)
Egg yolk 1	75.7 ± 0.1	72.3 ± 1.6	80.0	79.4 ± 1.1	99 ± 1.3
Egg yolk 2	80.6 ± 0.2	78.9 ± 2.1	80.0	82.6 ± 0.5	103 ± 0.6
Egg yolk 3	78.1 ± 1.1	75.2 ± 0.7	80.0	77.1 ± 0.2	96 ± 0.2
Egg yolk 4	67.5 ± 0.3	69.4 ± 1.3	60.0	59.1 ± 0.6	98 ± 1.0
Egg yolk 5	60.2 ± 0.7	57.9 ± 3.1	60.0	61.4 ± 0.9	102 ± 1.5

^a Mean ± SD of three measurements.

of •OH radicals in the presence of the DBS-LDH-Co(II)+H₂O₂+OH⁻ system may be responsible for the highly selective response of the present CL system towards Co(II). More interestingly, the developed CL sensitizer in this work can avoid serious interference from other metal ions generally encountered in the previous CL sensors for vitamin B₁₂ with the most common luminol reagent. Therefore, the DBS-LDH-Co(II)+H₂O₂+OH⁻ CL system can be applied to the specific determination of vitamin B₁₂ in egg yolk samples by liberating Co(II) with high sensitivity and selectivity. The obtained results of the proposed method were in good agreement with ones obtained by a standard ICP-MS method.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2014.05.041>.

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