Fe_3O_4 and bimetal–organic framework Zn/Mg composites peroxides-like catalyze luminol chemiluminescence for specific measurement of atropine in Datura plant

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Abstract

Atropine (AT) is a tropane alkaloid used as an anticholinergic drug. This substance is abundantly found in Datura plant seeds. In this work, Zn/Mg bimetallic MOF was integrated with Fe$_3$O$_4$, and Fe$_3$O$_4$@Zn/Mg MOF(Fe$_3$O$_4$@MOF) composite was synthesized. This compound has a high peroxidase-like activity based on the chemiluminescence (CL) reaction. The synergistic effect of Zn, Fe, and Mg metals in the Fenton reaction causes the production of reactive oxygen species (ROS), resulting in high CL intensity. Addition of AT quenching CL and thus AT can be measured. The linear range and limit of detection (LOD) of this method for measuring AT standard solution are 3-600µgL$^{-1}$ and 10 – 4µgL$^{-1}$, respectively. This method is easy, fast, reversible, selective, without biodegradability effects, low cost, high accuracy, and precision for measuring AT in the Datura plant.

Introduction

Datura is a plant of the Solanaceae family of about 9 to 12 species, Datura grows widely in temperate and warm regions[1]. This plant has been used as a poisoning agent and medicine in the southwestern United States and other parts of the world since 3000 years ago. The toxicity of Datura is due to the tropane alkaloids in it, which are found in abundance in the seeds, flowers, leaves, and roots of this plant[2]. Atropine is a toxic crystalline alkaloid that was named in the list of essential drugs of the Health Organization[3]. Atropine is used to treat diseases related to the pupil, hay fever, colds, intestinal spasms, and as an antidote to toxic gases and insecticides. However, the disadvantages of this drug in higher doses far outweigh the benefits and significantly expand the anticholinergic effect and psychiatric patients[4], [5].

Metal-organic frameworks (MOFs) have individual properties of high porosity, several composition, tunable pore structure, and multiple functionalities. Therefore, they have wide applications in different fields, especially catalysts like-peroxidase[6].

To date, atropine has been measured by luminescence methods including quantum data[4] and Zn/Co bimetal MOFs fluorescence [2], phosphorescence[7], electroluminescence (ELC)[8], and chemiluminescence (CL)[4], [9]. The CL analysis method has significant advantages of high sensitivity for detecting trace concentrations, fast response, low background signals with high stability, non-toxicity, wide dynamic range, and easy operation. In the absence of an external light source, they are widely used in biological sample measurement, food safety, and clinical diagnos[10]–[12]. CL signals are dependent on the reaction speed, so efficient catalysts change the signal intensity and increase the sensitivity of this measurement method[13]. Among the most significant nanocatalysts for the correction of CL, signals are improved monumental[12], [14]–[17] and bimetal MOFs[2], [18], [19] that are used as peroxidase-like catalysts. In this paper, Zn/Mg bimetallic MOF was integrated with Fe$_3$O$_4$, and Fe$_3$O$_4$@Zn/Mg MOF composite was synthesized. This compound has a high peroxidase-like activity based on the chemiluminescence reaction using the static composite-luminol-H$_2$O$_2$ method. The synergistic effect of Zn, Fe, and Mg metals in the Fenton reaction causes the production of reactive oxygen species ($\text{O}_2^\sigma$)
OH°), resulting in high CL intensity. Addition of AT quenching CL and thus AT can be measured. Factors affecting the catalytic activity of the composite (luminol concentration, H₂O₂, MOF, pH) were optimized using CCD statistical method scheme 1.

**Experimental**

**Device and materials chemistry**

Material chemicals used in the experiments were Magnesium nitrate hexahydrate (Mg(NO₃)₂.6H₂O), Zinc nitrate tetrahydrate (Zn(NO₃)₂.4H₂O), terephthalic acid (TA), Iron(II) chloride tetrahydrate (FeCl₂.4H₂O), Iron(III) chloride hexahydrate (FeCl₃.6H₂O), tetraethyl orthosilicate (TEOS), Sodium carbonate, epichlorohydrin, Hydrochloric acid(HCL) (37%), hydrogen peroxide(H₂O₂), Ammonia solution (32%), petroleum ethanol, Dimethylformamide (DMF), tetrahydrofuran(THF), thiourea, t-butyl alcohol, resazurin, para-benzoquinone, superoxide dismutase (SOD) and sodium azide, L-histidine, Dextrin were attained from Merck. Atropine, monosodium phosphate (NaH₂PO₄.H₂O) were gained from Sigma.

In the Fourier transform infrared (FT-IR) spectroscopy, samples were operating with KBr tablets, measured by device an AVATAR spectrometer (Thermo, America).

Thermal gravimetric analyses (TGA) utilized the model STA 504 BAHR (Thermo Analyse, Germany) at a heating rate of 10°C min⁻¹. We determined morphological characteristics by scanning electron microscopy, SEM (FEI, model Quanta 200, USA. X-ray diffraction (XRD) intensities measured by XRD model X’Pert Pro (PANalytical). Energy-dispersive X-ray spectroscopy (EDX) (FESEM, device model: MIRA II, SAMX detector made in France, Czech Republic). The produced CL signal was collected with luminometer device of Berthold company equipped with photomultiplier tube detector made in Germany.

**Preparation of Fe₃O₄ Nanoparticles**

22.5 mL of 0.12 M FeCl₂. 4H₂O and 22.5 mL of 0.2 M FeCl₃.6H₂O solutions were blended in a 250 mL two-mouth flask. The total reaction system was ended under current nitrogen at 60°C with a uniform speed of 15min stirring. 21.6 mL of 3M NaOH solution was added to the reaction system, then reaction at 60°C, 40min was performed. Then stirred the reaction system at 90°C for 30 min, and the resulting mixture cooled to room temperature. The dark sediment was assembled by magnetic and washed with deionized water/ethanol with (5:1v/v) three-time. The received dark residue dried over a vacuum at 30°C overnight[20], [21]

**Preparation of Fe₃O₄@SiO₂**
Modification of Fe$_3$O$_4$ Nanoparticles with TEOS: 30mg of Fe$_3$O$_4$ synthesized acidized by HCl (0.1 mol/L) ultrasonic for 20 min. Using a magnet, discard the supernatant; residual was washed with DDW three times, then added DDW/ethanol (60:40 v/v) to sample that MNPs suspension. Ammonia (NH$_3$.H$_2$O) (750µl) was increased to Fe$_3$O$_4$, and the compound was reacted to for 20 mines under the ultrasound at 40°C. TEOS (96µL) was attached to the samples. Then the examples oscillated at 140 r/min for three hours, MNPs sorption by the magnet. The supernatant was throw away, and the sediment was washed with DDW/ethanol three times to yield Fe$_3$O$_4$@SiO$_2$[22].

**Synthesis bimetal Zn/Mg MOF**

To synthesize Zn/Mg MOF (Zn:Mg ratio of 1:1), dissolve 1.8g Zn(NO$_3$)$_2$.4H$_2$O, 1.5g Mg(NO$_3$)$_2$.6H$_2$O, and 1.7g TA in 80ml DMF for 15min, add 0.5 ml HCl (3mmol) to the solution and after 60 min stirring, mix for 24h at 120°C in the autoclave. Cool the sample gently at room temperature. Separate the solvent from the sediment by centrifugation (8000 rpm, 10 min), wash the precipitate twice with DDW and ethanol for 12h, and finally store in ethanol for 24h. Then collect the precipitate Zn/Mg MOF by centrifugation and dry overnight in a vacuum oven (37°C).

**Preparation hybrids Fe$_3$O$_4$@SiO$_2$/MOF, Fe$_3$O$_4$@MOF**

These composites were synthesized: 0.05 g Fe$_3$O$_4$@SiO$_2$ or Fe$_3$O$_4$, 0.5g Mg(NO$_3$)$_2$.6H$_2$O, 0.5g Zn(NO$_3$)$_2$.4H$_2$O in 40ml DMF were ultrasonic for 60min and solution TA (0.5g TA + 40ml DMF) was added to it, and 24h at 120°C in autoclave then precipitated slowly at room temperature, centrifugation precipitate and washed twice for 12h with DMF washes. Precipitate collected by centrifugation and dried in a vacuum oven for 24h, 36°C.

**Synthesis hybrids Fe$_3$O$_4$@SiO$_2$/MOF/ Dextrin, Fe$_3$O$_4$@MOF/Dextrin**

For the synthesis of these composites, 0.5g Fe$_3$O$_4$@SiO$_2$/MOF or Fe$_3$O$_4$@MOF, 40ml DMF, 1.2g Dextrin, 4g sodium carbonate, and 0.6g cross-linker epichlorohydrin under nitrogen gas, 85°C, 24 hours reaction performed. The product is a suspension that cooled to room temperature. The precipitate is filtered and washed three times with DMF and THF and dried in a vacuum oven (50°C).

**AT measurement method in CL process**

In this process 0.2ml of 1µM H$_2$O$_2$ solvent and 0.5ml of 0.1mgml$^{-1}$ MOF solvent using phosphate buffer (pH = 7) increased to a volume of 1ml, The CL reaction was then started by injecting 0.5 ml of 50µM
luminol in the presence or absence of atropine (0.5ml, 10^{-2}µgL^{-1}) and the curve CL = CL₀-CLₐ/ CL₀, (CL₀ reaction in the absence of atropine and CLₐ reaction in the presence of atropine) were plotted in time.

**Optimization of peroxidase-like activity conditions of composite in CL reaction**

Response surface methodology (RSM) was used to optimize CL reaction conditions in Atropine measurement. RSM is a set of mathematical and statistical techniques used to construct a laboratory model, which goal is to find the best answer generated under the influence of several independent variables. In this study, compound central design (CCD), the most common type of RSM, was used to evaluate the effect of independent variables: Luminol concentration, H₂O₂, MOF, pH on two levels with minitab17 software. Table 1 shows the variables and CCD level for the CL test.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Unit</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low(-1) High(+1)</td>
</tr>
<tr>
<td>pH (X₁)</td>
<td>-</td>
<td>9 11</td>
</tr>
<tr>
<td>concentrations MOF(X₂)</td>
<td>mg/ml⁻¹</td>
<td>10 15</td>
</tr>
<tr>
<td>concentrations H₂O₂(X₃)</td>
<td>µM</td>
<td>5 10</td>
</tr>
<tr>
<td>concentrations luminol(X₄)</td>
<td>µgL⁻¹</td>
<td>30 50</td>
</tr>
</tbody>
</table>

**Result**

**Characteristics of synthesized composites of MOF**

Figure S1 shows the spectrum obtained from FT-IR for bimetallic MOF and MOF-derived composites. The scattering of the Zn^{+2} / Mg^{+2} bimetallic MOF peaks according to reference [23] in the range 470-1700 cm⁻¹ is observable. The sharp and weak peaks in the region of 427–527 cm⁻¹ correspond to the oxides of Zn-O and Mg-O metals attached to the ligand, respectively. The peaks in the 685–826 cm⁻¹ region are related to the bending vibrations of the C-H ring-in-and-out bond in TA. The sharp peaks in 1546–1698 cm⁻¹ and 1383–1439 cm⁻¹ describe asymmetric and asymmetric stretching vibrations of the carboxyl group in the TA ligand bridged between Mg^{2+} and Zn^{2+}. Very weak peaks in the 2583 and 3098 cm⁻¹ regions belong to the methyl group in the DMF solvent. The weak peak in the area of about 2000 cm⁻¹ is related to the metal Mg^{+2} attached to TA. this peak is very weak and indicates the connection of a small percentage of metal Mg^{2+} is with TA, and a higher percentage of Mg^{2+} is
associated with TA which acts as a bridge between the two metals Mg$^{2+}$ and Zn$^{2+}$ [24]. All spectra except MOF, approximately wide peaks in the region of 3400 cm$^{-1}$ and 495-598 cm$^{-1}$ interrelated to the stretching vibrations of O-H and Fe-O, respectively. In composites containing SiO$_2$ in the range of 2900 cm$^{-1}$, 950 cm$^{-1}$, 1024 and 750–800 cm$^{-1}$, near 492 cm$^{-1}$, it is related to aliphatic C-H bond in methyl and propyl groups, Si-OH, Si-O-Si, and Fe-O-Si, respectively.

The peaks seen in the range of 3000 cm$^{-1}$, 1300 cm$^{-1}$, and 1180 cm$^{-1}$ are related to the stretching vibrations of C-H aromatic, C-C, and C-O related to Dextrin, respectively, which are well in the range of composites with Dextrin seen.

Morphological surface, porous structure of materials, composite sizes check using the scanning electron microscope. Figure 1 shows a clear picture of SEM for Zn$^{2+}$/Mg$^{2+}$ bimetal MOFs and their composites. These composites have an irregular but porous structure.

Figure S2 shows the TGA curve for composites synthesized from A-E. For composite A at 112.8-184.8 °C, B at 103.3-274.4 °C, D at 77–240 °C and E at 110–175 °C represents A-E with weight loss of 16.85%, 21%, 26.81%, 24.3%, 11.33% for solvent, respectively. With increasing temperature, degradation of the ligand and the structure of the composites from A-E at temperatures above 370 °C, 420 °C, 460 °C, 350 °C, 340 °C performed.

Figure S3 demonstrates the composites and MOF bimetal elemental analysis energy-dispersive X-ray spectroscopy (EDX). In this analysis, the ratio of Zn to Mg for A-D composite and bimetal MOF is 4.51:3.7, 6.32:7.57, 3.05:2.51, 6.9: 7.63, 5.77: 4, respectively. Confirms the ratio of Zn to Mg atoms of approximately 1:1 in these composites.

Table S1 shows the surface area, pore volume, and pore diameter BET for the composites. The observed decrease in surface area E to A composite is due to the closure of the pores in the MOF bimetallic by molecules Dextrin and SiO$_2$.

**Optimization of peroxidase-like activity conditions of composites in CL reaction**

In this experiment, four factors effectively were optimized via CCD. All factors were defined at two levels (+1, -1), there included 31 thighs with $\alpha = 2.5$. Four variables effectively and independently were used in the CCD model presented in Table S2. Table S3 is related to ANOVA, which shows the fit of the experimental data of the model used with the predicted data.

Based on the results ANOVA p-value < 0.05 significant parameters indicate a 95% confidence level. R$^2$ and R$^2$-adjusted for the model are 97.73% and 95.74%, respectively. These data confirm the degree of accuracy and correlation between the predicted responses and the experimental data obtained. The lack
of fit (LOF) p-value of 0.32, this issue is more than 0.05% and indicates the compatibility of the model with the data.

The regression equation for this model is as follows, this model includes the main factors and binary interaction between the main factors:

\[
\text{CL} = -38581739 + 282419 X_4 + 549258 X_3 + 781237 X_2 + 5418765 X_4^2 - 37468 X_3^2 - 35742 X_2^2 - 244281 X_1^2 + 1699 X_4 X_3 + 1692 X_4 X_2 - 11263 X_4 X_1 + 11616 X_3 X_2 - 16606 X_3 X_1 - 1998 X_2 X_1
\]

Based on these results, the optimal values are for Luminol concentration 41.82µM, H\textsubscript{2}O\textsubscript{2} 8.2µM, MOF 13mL\textsuperscript{-1}, pH 9.8. Figure S4 displays the response surface diagram for each pair of factors.

Mechanism of the Peroxidase-like activity of composite in CL reaction

Scavenger compounds are used in the composite-Luminol-H\textsubscript{2}O\textsubscript{2} system for the routine detection of reactive oxygen species (ROS) in CL reactions.

the effect of different radical scavengers, including thiourea, t-butyl alcohol, and resazurin (scavengers of OH\textsuperscript{o}), para-benzoquinone, superoxide dismutase (SOD) and sodium azide (scavengers of O\textsubscript{2}\textsuperscript{-}), and L-histidine and DMF (scavengers of \textsuperscript{1}O\textsubscript{2}), on the CL emission intensity has been investigated and the results are listed in Table 3.

Figure 2 shows the diagram of the inhibitory effect compounds on the intensity of CL.
Table 3  
the effect of different radical scavengers on the in the composite-Luminol-H$_2$O$_2$ system.

<table>
<thead>
<tr>
<th>Scavengers</th>
<th>Intermediate</th>
<th>Concentration</th>
<th>Percent quenching(%)</th>
</tr>
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<tbody>
<tr>
<td>thiourea</td>
<td>OH$^\circ$</td>
<td>1mM</td>
<td>91</td>
</tr>
<tr>
<td>t-butyl alcohol</td>
<td>OH$^\circ$</td>
<td>0.2mM</td>
<td>85</td>
</tr>
<tr>
<td>resazurin</td>
<td>OH$^\circ$</td>
<td>2.5µM</td>
<td>81</td>
</tr>
<tr>
<td>para-benzoquinone</td>
<td>O$_2^\sigma$</td>
<td>0.3mM</td>
<td>71</td>
</tr>
<tr>
<td>SOD</td>
<td>O$_2^\sigma$</td>
<td>4mgml$^{-1}$</td>
<td>80</td>
</tr>
<tr>
<td>sodium azide</td>
<td>O$_2^\sigma$</td>
<td>10mM</td>
<td>67</td>
</tr>
<tr>
<td>L-histidine</td>
<td>O$_2^\sigma$</td>
<td>10mM</td>
<td>19</td>
</tr>
<tr>
<td>DMF</td>
<td>$^{1}$O$_2$</td>
<td>0.5M</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>$^{1}$O$_2$</td>
<td></td>
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</tbody>
</table>

The possible mechanism is caused by the reaction of H$_2$O$_2$ in an alkaline environment and the presence of Fe$_3$O$_4$@Zn/Mg composites. Due to their multivalent states, iron and zinc metals participate in the Fenton reaction and produce active species O$_2^\sigma$, OH$^\circ$ for peroxidase-mimic activity:

$$\text{Fe}^{2+/Zn^+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+/Zn^{2+}} + \text{OH}^\circ + \text{OH}$$ (1)

$$\text{Fe}^{3+/Zn^{2+}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+/Zn^+} + \text{HO}_2^- + \text{H}^+$$ (2)

$$\text{Fe}^{3+/Zn^{2+}} + \text{HO}_2^- \rightarrow \text{Fe}^{2+/Zn^+} + \text{H}^+ + \text{O}_2^\sigma$$ (3)

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$$ (4)

$$\text{HO}_2^- + \text{OH}^\circ \rightarrow \text{H}_2\text{O} + \text{O}_2^\sigma$$ (5)

Mg metal has high ionization properties. The synergy of Mg in the composite provides necessary electrons for the generation of more Fe$^{2+/Zn^+}$, accelerates the Fenton reaction, and produces ROS. Based on Fig. 3, Luminol(L) has converted to Luminol anion (L$^\neg$) in an alkaline medium. L$^\neg$ produces the compound 3-aminophthalate anion (AP$_2^{2-}$) * due to contact with ROS, which has CL by returning to the base state at $\lambda = 425$.

In the presence of atropine, due to the binding AT with composite, a few numbers of O$_2^\sigma$, OH$^\circ$ radicals are produced to the peroxidase-like activity. As a result, the intensity of CL decreases.
To better understand the catalytic effect of Fe$_3$O$_4$@MOF composite in the CL system and atropine measurement, the intensity difference CL of the compounds following in the presence and absence of atropine was investigated. According to Fig. 4, CL intensity decreased in all nanoparticles with the presence of atropine. But in the Fe$_3$O$_4$@MOF nanoparticle, a high decrease is visible. This intensity reduction shows the high catalytic activity of the composite in the production of ROS and the numerous ability to measure atropine.

**Method validation**

To determine the validity of this method in measuring atropine, First, the atropine calibration curve in solutions with standard concentrations (3-600 µgL$^{-1}$) plotted by the peroxidase-like activity of the Fe$_3$O$_4$@MOF composite based on the CL experiment in Fig. 5.

The linear range for measuring atropine is approximately 3-600µgL$^{-1}$. Regression equation $\Delta$CL $= 10258x + 23503$ (slope of calibration curve $m = 29309$, the standard deviation of $S_b$ blank solution with concentration 1µgL$^{-1}$ for six repetitions in measuring CL intensity 1.02% Was registered).

LOD, LOQ and $R^2$ were calculated to be $10^{-4}$µgL$^{-1}$, $4\times10^{-4}$µgL$^{-1}$ and 0.9831, respectively.

**Selectivity and stability of the catalytic activity of the composite**

Selectivity, stability, and repeatability are important offices of the CL method in measuring specific analytes. Selectivity and stability indicate the practicality of selecting and resisting the catalyst in measuring the desired analyte in an environment containing different compounds. The selectivity of this method was investigated by CL response to luminol - H$_2$O$_2$ - Fe$_3$O$_4$@MOF composite system for different species in the presence or absence of atropine. In Fig. 6, the selectivity of this method for estimating atropine is well evident. In the absence of atropine, the CL intensity of all compounds is approximately identical but decreases CL intensity with AT.

Cyclic CL tests were performed to check the stability and reversibility of composite Fe$_3$O$_4$@MOF. After each cycle CL experiment, the composites were separated from the solution using a centrifuge (8000rpm, 8min). MOF was washed five times with methanol: DDW (4:1v/v), then dried overnight at 37°C temperature in a vacuum oven. The composites were used again for the same reaction. This cycle was repeated 10 times. The composites have nearly the same responses for five thighs. It can be recoverable with the same sensitivity for five thighs and gradually lose its proficiency.

Activity efficiencies for thighs 6, 8, and 10 are 90.46%, 85.5% and 37.2% individually.
Determination AT in real Datura sample:

0.5g of dried defatted samples were ultrasonic with 30ml methanol for 60 mines. The extract was separation by paper filtration. The solvent was deleted by rotary; the temperature is not more than 40°C. To dried extract of the flask was added 50 mL of 5% hydrochloric acid with ultrasonic. The aqueous acid phase was extracted with 3 × 40 mL DCM. The organic phase was discarded at the bottom of the decanter. The aqueous extract phase's pH reached pH 10 with ammonium hydroxide (25% NH4OH) then Atropine was extracted with 5 × 40 mL of DCM. The organic phase is separated and dried with 30 g of anhydrous sodium sulfate; then, it filtration through filter paper. The solvent was deleted by rotary. The dry extract of Atropine was solubilized in 1ml DDW. Finally, atropine extracted by the LLE method from the seeds of two types of D. innoxia and D. Stramonium native to the north and west of Iran was measured by this method. The results obtained for sample D. Innoxia north and west of Iran and D. stramonium north and west of Iran were published 102.30 µgL\(^{-1}\), 100.67µgL\(^{-1}\), 22.8 µgL\(^{-1}\), 13.4 µgL\(^{-1}\), sequentially.

Conclusion

In this paper, Zn/Mg bimetal MOF was integrated with Fe\(_3\)O\(_4\), and Fe\(_3\)O\(_4\)@MOF composite was synthesized by the hydrothermal method. Based on CL reaction, AT was measured in the Datura plant. This composite has a high peroxidase-like activity, due to the production of active radicals (O\(_2\)º̄, OHº) and has a high CL intensity. In the presence of AT, this substance is selectively attracted to the surface of metals and ligands, result CL intensity decreases. Effect factors related to the catalytic activity of the composite optimized by the CCD statistical method. The linear range, LOD, and LOQ for measuring the standard solution of atropine in this method are estimated at 3-600µgL\(^{-1}\), 10\(^{-4}\)µgL\(^{-1}\), 4×10\(^{-4}\) µgL\(^{-1}\), respectively. This method is a fast, simple, selective, and safe method of determination of AT in two types of Datura plants (D. Innoxia and D. stramonium) using.

References


**Scheme 1**

Scheme 1 is available in the Supplementary Files section.

**Supplementary Table And Figure**

Supplementary Tables S1-S3 and Figures S1-S4 are not available with this version

**Figures**
Figure 1

SEM images of a) Fe$_3$O$_4$@SiO$_2$/MOF/Dextrin, b) Fe$_3$O$_4$@SiO$_2$/MOF, c) Fe$_3$O$_4$@ MOF/Dextrin, d) Fe$_3$O$_4$@ MOF, e) Zn$^{2+}$/Mg$^{2+}$ bimetallic produced.
Figure 2

effects of different scavengers on the CL intensity of 0.2ml H$_2$O$_2$ (1µM), 0.5ml composite (0.1mgml$^{-1}$), 0.5 ml luminol (50µM).
Figure 3

Reaction CL based on Luminol-H$_2$O$_2$
Figure 4

Difference intensity CL in the presence and absence of 10^{-2} \mu\text{gL}^{-1} atropine, 0.2ml H_2O_2 (1\mu M), 0.5ml composite (0.1mgml^{-1}), 0.5 ml luminol (50\mu M).
Figure 5

CL spectra of lumiol-$\text{H}_2\text{O}_2$-$\text{Fe}_3\text{O}_4$@MOF composite solution in the presence
Figure 6

The response of luminol-H$_2$O$_2$-$\text{Fe}_3\text{O}_4$@MOF composite solution for different compounds in the absence or presence of atropine (optimum condition, atropine concentration is 100µgL$^{-1}$, concentrations of other compounds are 30 time more than atropine, 0.2ml H$_2$O$_2$ (1µM), 0.5ml composite (0.1mgml$^{-1}$), 0.5 ml luminol (50µM), [S: main system, 1–24: leucine, glycine, L-histidine, L-serine, ascorbic acid, ampicillin, amoxicillin, alanine, L-cysteine, L-valine, codeine, l-arginine, cephalexin, vitamin B2, L-lysine, glutathione, ibuprofen, methadone, glucose, lactose, uric acid, scopolamine, dopamine respectively].

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- scheme1.png