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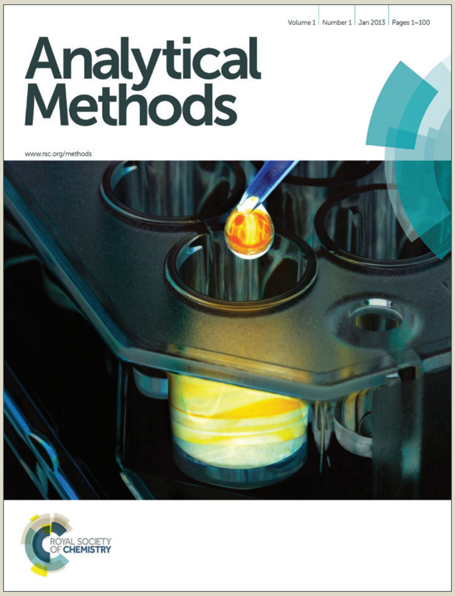

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A novel chemiluminescence sensor for determination of vanillin with graphene oxide-magnetite-molecularly imprinted polymers

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Abstract

A novel chemiluminescence (CL) sensor for the on-site determination of vanillin using the system of luminol-$KMnO_4$-NaOH based on magnetic graphene oxide-molecular imprinted polymer (GM-MIP) was described. The vanillin-GM-MIP with merits of easy separation, high selectivity and large amount of adsorption was synthesized as vanillin recognition material in the CL analysis and the GM-MIP column was placed in front of the pump to increase the selectivity of CL analysis. The GM-MIP was characterized by SEM, XRD, TEM and FTIR, and also for the adsorption ability, selectivity and reusability. The GM-MIP-CL sensor responded linearly to the concentration of vanillin over the range of 3.3×10^{-7} - 1.2×10^{-5} mol/L with detection limit of 1.1×10^{-7} mol/L (3δ). The RSD was 3.9%, and on the basis of speediness and high selectivity, the sensor showed a great improvement in selectivity and adsorption capacity. Finally, the sensor had been applied for the determination of vanillin in practical samples, and the recoveries were between 6%-8%. The sensor was easily-get, simple, automatically column packing and high selectivity.

Keywords: chemiluminescence, vanillin, magnetic graphene oxide, molecularly imprinted polymer, column packing

1 Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde), a flavoring component widely used in foods, beverages, cosmetics and drugs, was regarded that the high level of it would be harmful to human health. Currently, the reported methods in the detection of vanillin were electrochemical method [1], high-performance liquid chromatography [2], gas chromatography [3], capillary electrophoresis [4] and UV-vis spectrophotometry [5].

Though most of mentioned methods offered helpful information in terms of quantitation, excellent resolution and selectivity, they required highly expensive or sophisticated instruments and involved in complicated sample pretreatment processes while the others suffered from low selectivity.

CL, being a promising method in determination of practical samples, was well known as a powerful analytical technique that possessed of high sensitivity, wide linear range, rapid determination and simple instrument [6] and has been applied in enzyme immunoassay [7], biomedical [8], food analysis [9], pharmaceutical [10] and agriculture [11]. Luminol CL detection [12, 13] offered an advantage in CL imaging and integrated determination by the virtue of its stable CL and high quantum yield but the method was limited in development and application for its poor selectivity.

To overcome the difficulty of poor selectivity of CL, MIP was employed based on its high selective recognition and capture capabilities. To prepare MIP, two different approaches have been developed: covalent interactions [14] and non-covalent interactions [15] between template molecules and monomers. The molecularly imprinted technology (MIT) has been applied in fluorescent organic compounds' detection [16], antibody binding [17], enzyme mimics [15] and biomimetic sensors [18]. Even so, MIP suffered from difficult separation and low adsorption capacity.

Magnetite (Fe_3O_4) nanoparticles (NPs) possessed excellent easy to separate, controlled particle size, stable physical properties and low toxicity, low cost, and eco-friendliness which served as a stabilizer and segregator and had promising applications in catalysis, biomedicine, spintronics and magnetic recording devices [19].

Graphene oxide (GO) has attracted considerable attention in recent years [20] for its unique two-dimensional structure and extraordinary properties and held great promise for potential applications in nanomaterials and nanotechnology [21]. So far, chemical modification and functionalization of graphene oxide has focused on incorporating a composite material [22-25] on graphene sheets cted unique properties and wide applications of graphene oxide-Fe_3O_4 (GM) composite have been explored.

In this work, a novel GM-MIP-CL sensor for vanillin determination was developed. In the preparation of GM-MIP, MIP was introduced into CL to improve selectivity and the addition of the vanillin could be recognized in a mixture reaction consisting of a cross-linker, a solvent, and a functional monomer [26], GO was employed to improve the adsorption capacity for its high surface area and Fe_3O_4 nanoparticles were applied not only to separate and immobilize easily but also to pack column firmly. Because of the existence of three-dimensional special recognition sites on the GM-MIP, the vanillin could be selectively adsorbed by MIP effectively, greatly improved the selectivity of CL analysis. The adsorption capacity, selectivity and reusability of the vanillin-GM-MIP were studied. Under the optimal CL conditions, the GM-MIP-CL sensor was successfully used in determining vanillin in food samples with an easy-get, simple and automatical column packing and the sensor showed very selectivity to vanillin.

2 Experiment

2.1 Chemicals and materials

Vanillin (A.R) was purchased from Sinopharm Chemical Reagent Co. Ltd.; Acrylamide (A.R) was purchased from Tianjin Chemical Reagent Co. Ltd.; Ethylene glycol dimethacrylate (EGDMA, A.R) was supplied from Aladdin Reagent Co. Ltd.; 2,2-azobisisobutyronitrile (AIBN, A.R) was supplied from Sigma-Aldrich. The ethanol, acetic acid, sodium hydroxide, potassium permanganate and all other chemicals unless specified were of analytical reagent grade and used without further purification.

EGDMA was distilled to remove inhibitors. AIBN was recrystallised prior to its use.

The vanillin stock solution (1.0×10^{-2} mol/L) was prepared by water as solvent. Luminol stock solution (1.0×10^{-2} mol/L) was prepared by alkaline solution as solvent and stored in refrigerator (4°C).

Redistilled water was used throughout the work.

2.2 Apparatus

The IFFM-E flow injection CL analyser (Xi'an Remex Electronic instrument High-Tech Ltd., China) was equipped with an automatic injection system and a detection system. PTFE tubes (0.8 mm i.d.) were used to connect all of the components in the flow system. Glass capillary filling with MIP and nonmolecularly imprinted polymer (NIP) were positioned in front of the flow injection-CL (FI-CL) analyser. A switch walve was used to change the flow direction. The CL signal was recorded by a computer and the data was disposed by the software. The schematic diagram of sensor used in this work was shown in Fig. 1.

Glass capillaries (i.d. 1.0 mm, L. 100 mm) were from West China University of Medical Sciences Instrument Factory.

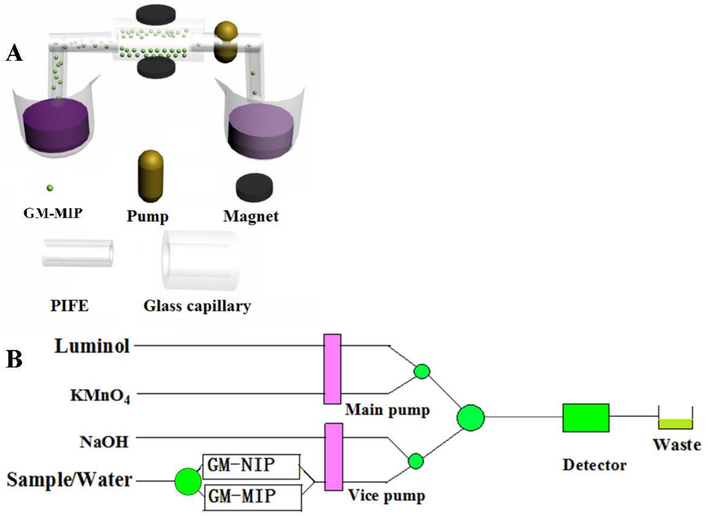


Fig. 1. The schematic diagram of vanillin-GM-MIP sensor. (A) The schematic of wet column packing; (B) The mechanism of CL sensor based on MIP column

2.3 Preparation of GM-MIP and GM-NIP

Graphite oxide was prepared from nature graphite powders by a modified Hummers method [27] and reported article [28].

Firstly, 120 mL H_2SO_4 (95%) was added into a 500 mL flask, and then cooled by immersion in an ice bath followed by stirring. Subsequently, 5.0 g graphite powder and 2.5 g $NaNO_3$ were added under vigorous stirring to avoid agglomeration. After the graphite powder was well dispersed, 15 g $KMnO_4$ was added gradually under stirring and the temperature of the mixture was kept to be below 10˚C by ice cooling. Secondly, 150 mL of H_2O was slowly added to the paste with vigorous agitation. The diluted suspension was stirred at 98˚C for 1 day. Then, 50 mL 30% H_2O_2 was added to the mixture. Finally, the mixture was filtered and washed with 5% HCl aqueous solution followed by water until the pH was 7.0. After filtration and drying at 65˚C under vacuum, graphite oxide was obtained as gray powder.

GO nanosheets were prepared according to the previous literature [29].

Graphite oxide powders were dispersed in water to create a 0.05 wt.% of dispersion.

Exfoliation of graphite oxide to GO was achieved by ultrasonication for 1 h, in which the bulk graphite oxide powders were transformed into GO sheets. The obtained brown dispersion was then subjected to 30 min of centrifugation at 3000 r.p.m. to remove any unexfoliated graphite oxide. The final products were then centrifuged, washed with water, and finally dried under vacuum at room temperature.

The magnetic graphene oxide composites (GM) were synthesized according to the methods of our group [30].

The GM were synthesized by the insitu chemical coprecipitation of Fe^{2+} and Fe^{3+} in alkaline solution in the presence of GO. The magnetic composite was prepared by suspending 0.5 g GO in 200 mL of solution containing 1.7 g (4.33 mmol) $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 2.51 g (8.66 mmol) $NH_4Fe(SO_4)_2{\cdot}12H_2O$ at 50˚C under N_2 atmosphere. After the solution was sonicated (200 W, 40 kHz) for 10 min, 10 mL of 8 mol/L NH_4OH aqueous solution was added drop wise to precipitate the iron oxides while the mixture solution was sonicated. The pH of the final mixture was 11.5. To promote the crystallization of complete growth of the nanoparticles, the reaction was carried out at 50˚C for 60 min under constant mechanical stirring. The precipitate was isolated in the magnetic field. The impurities in the GM samples were removed by washing with double-distilled water and isolated. The obtained GM composites were then washed with 150 mL of absolute alcohol for three times. Subsequently, the composite was dried under vacuum.

A typical preparation of the MIP was carried out as article reflex [28, 31]. MIP were prepared using vanillin as template, AM as functional monomer and EGDMA as cross-linker. A 25 mL ethanol solution containing 0.1 mmol Vanillin, 0.4 mmol AM was prepared. After degassing and nitrogen purging for about 5 min to remove oxygen which inhibited the polymerisation, the solution was placed at 25˚C for 12 h. Then 0.2 g silanizated magnetic nanoparticles were added into the solution, sonicating for 5min and then shaked at 25˚C for 12 h. 2.0 mmol EGDMA and 20 mg AIBN were added into the solution which was continued shaking for 24 h at 60˚C. Then the polymers were extracted with methanol/acetic acid (9/1, *V*/*V*) overnight and washed with double-distilled water to remove any non-grafted polymer, monomer, residual initiator and the template.

The magnetic graphene oxide-nonmolecularly imprinted polymer (GM-NIP) was prepared and processed in the same way, but in the absence of any template.

The procedures were shown in Fig. 2.

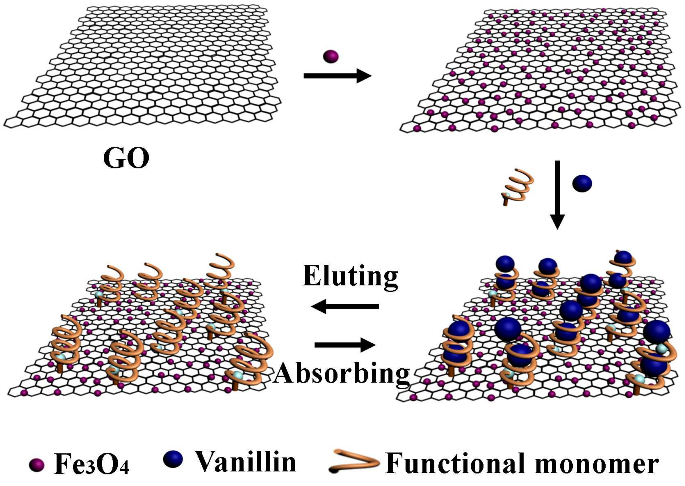


Fig. 2. Synthetic process of GM-MIP.

2.4 Adsorption performance

The adsorption capacity of GM-MIP and GM-NIP for vanillin was investigated as follows: 20.0 mg of GM-MIP (GM-NIP) was mixed up with 10.0 mL of vanillin solution in a 50 mL iodine flask and oscillated 24 h for adsorption.

2.5 The GM-MIP-CL sensor

An easy-get, simple and automatical column packing was prepared as following：40 mg GM-MIP (GM-NIP) particles eluted template molecules were dispersed in 100 mL water with ultrasonication, and then the dispersed liquid were injected to the capillary (id. 4 mm, L. 10 cm) using flow injection pump. Under the action of magnetic field, the GM-MIP was fixed in the capillary wall, as shown in Fig. 1(A).

The capillary was placed in front of the FI-CL analyser as recognition elements. The sensing mechanism of the CL sensor based on MIP column was showed in Fig. 1(B), In order to obtain good stability, the instrument was run for at least 10 min before the first measurement.

2.6 Procedures for determination

The schematic of the FI-CL sensor shown in Fig. 1 was used to optimize the reagents concentrations and determine the objective components in the water samples. The determination process included four steps: MIP CL value I_0, NIP CL value I_s, CL value ΔI and the GM-MIP column cleaning. The main pumps and the vice pump were started all the time.

(1) Sampling valve was in the sampling position. The reversing valve was connected with the MIP column. The vanillin solution were transmitted by the vice pump to flow through the MIP column, the vanillin in the solution were completely absorbed by MIP column. Luminol, potassium permanganate and hydrogen peroxide solution and unadsorbed vanillin solution were mixtured to react, producing CL value I_0.

(2) The reversing valve were connected with the NIP column, the vice pump transmitted vanillin solution to flow through the NIP column, and the vanillin could not be adsorped. Luminol, potassium permanganate and hydrogen peroxide solution and the solution containg vanillin were in the reaction, producing CL value I_s.

(3) The CL value of vanillin was obtained: $\Delta I = I_s - I_0$. According to regression equation, calculate the concentration of vanillin.

(4) The sampling valve was in the sampling position, the main pump and vice pump transmitted the deionized water flowing through the MIP and NIP column, washing the MIP and NIP column to use again. After the entire test, the apparatus was washed and emptied.

3 Results and discussions

3.1 Characterization of GO, GM, GM-MIP and GM-NIP

Representative Transmission Electron Microscope (TEM) images of the obtained GO and GM were showed in Fig. 3. It can be seen that GO was a thin piece layer of fold, which confirmed the GO was prepared successfully. And also as shown in the figure, Fe_3O_4 NPs have been coated on the GO surface.

Scanning Electron Microscope (SEM) images of the obtained GO (a) and GM (b) were shown in Fig. 4. We could get that GO was a fold of thin monolayer structure, while on the surface of GM, as seen, Fe_3O_4 NPs were stably attached to the surface of GO through chemical bonding. Fig. 5 indicated that the surface of MIP (a) was rough and uneven while the surface of NIP (b) was smooth, and it greatly confirmed the modification of GM with MIP.

Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin-Elmer instrument with the sample incorporated in KBr pellet. The nature of the chemical groups on surface of GO, GM, MIP and NIP were investigated by FTIR spectra shown in Fig. 6. In the spectrum of GO, the peak at 1640 cm^{-1} was attributed to C=O group stretching vibration. Bands at 1600 cm^{-1}-1400 cm^{-1} are the characteristics of benzene ring. The peak at 1000 cm^{-1} was the characteristic of C-OH bonding, which confirms the presence of GO. In the spectrum of GM, the peak at 620 cm^{-1} was the characteristic of Fe_3O_4, which provided a solid support that GM was prepared successfully. In the spectrum of MIP, compared with NIP, the absorption peak at 3000 cm^{-1} was more stronger, which revealed the MIP were prepared satisfactorily.

Also shown in Fig. 7 (A), there was one peak for GO: 10.7°, six peaks for Fe_3O_4: 30.2°, 34.9°, 42.9°, 56.8°, 53.3° and 62.3°, while GM had 7 peaks: one peak was for GO and the other six were the characteristic peaks of Fe_3O_4. Fig. 7 (B) showed that GM was absorbed by external magnetic field which indicated the GM was of high magnetism.

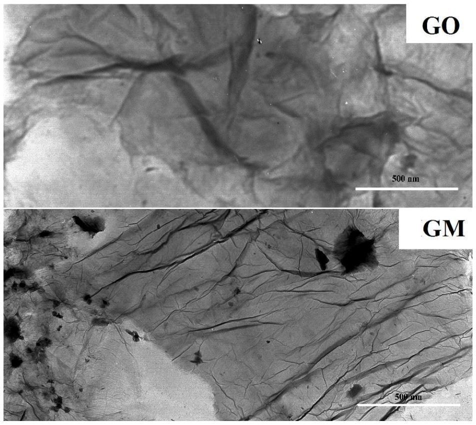


Fig. 3. The TEM images of GO (a) and GM (b)

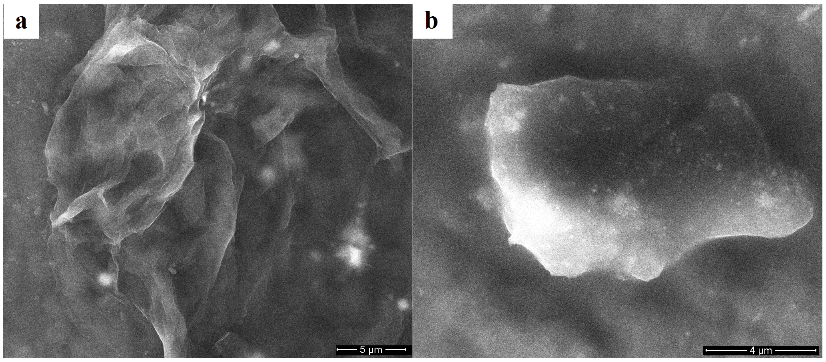


Fig. 4. SEM images of GO (a) and GM (b)

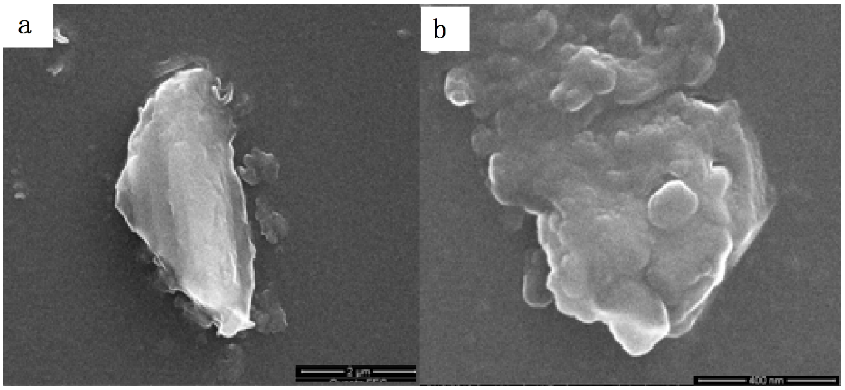


Fig. 5. The SEM of GM-NIP (a) and GM-MIP (b)

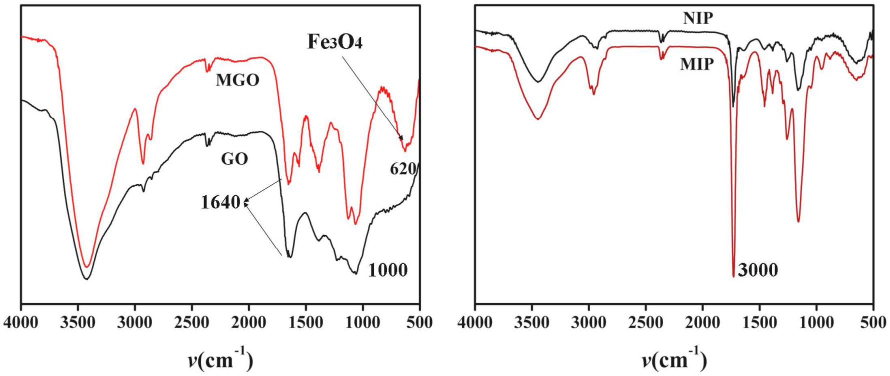


Fig. 6. The FTIR spectra of GO, GM, GM-MIP and GM-NIP

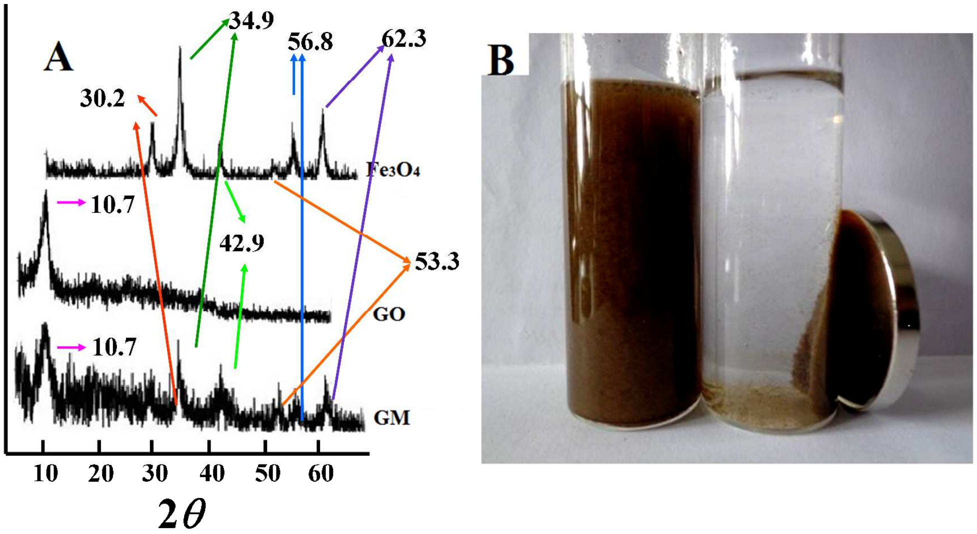


Fig. 7. The XRD of Fe_3O_4, GO, GM (A) and the magnetism of GM (B)

3.2 Adsorption performance of GM-MIP and GM-NIP

The adsorption capacity (Q) was calculated by Eq. 1.

$$Q = \frac{(c_0 - c_e) \times V}{m} \quad \text{Eq.1}$$

Where c_o and c_e (mol/L) were the initial concentration of vanillin in solution and supernatant respectively, V (L) is the volume of the initial solution and m (g) was the mass of GM-MIP or GM-NIP.

The Q of vanillin on the maximum adsorptions of GM-MIP and GM-NIP were 4.188×10^{-5} mol/g and 1.082×10^{-5} mol/g. For imprinted cavities on the surface of MIP, the target molecules were highly adsorbed by GM-MIP, but on the contrary, poor adsorption performance was observed for GM-NIP without imprinting cavities. The results demonstrated that the GM-MIP was suitable for use in CL sensor.

3.3 The optimization of CL reaction conditions

The schematic of the CL sensor shown in Fig. 1 was used to optimize the reagents concentrations for the CL determination of vanillin. With the main pump speed ranging from 20 to 40 r/min, the CL intensity increased by raising main pump speed up to 30 r/min. Above 30 r/min, the CL intensity decreased. Thus, the 30 r/min of main pump speed was used for further work. The effect of vice pump speed was examined from 20 to 40 r/min, the CL intensity reached maximum when vice pump speed was 30 r/min. The CL reaction reagent concentration optimization results were shown in Fig. 8(A-E).When $c(\text{KMnO}_4)$ was 3.0×10^{-5} mol/L, c(NaOH) was 0.2 mol/L and c(luminol) was 7.0×10^{-5} mol/L respectively, the CL intensity reached maximum which would improve sensitivity. The best CL reaction conditions were chosen for the next experiments.

3.4 The analytical performance of GM-MIP sensor

Under the optimal experimental conditions described ($c(\text{KMnO}_4) = 3.0 \times 10^{-5}$ mol/L, $c(\text{NaOH}) = 0.2$ mol/L, $c(\text{luminol}) = 7.0 \times 10^{-5}$ mo/L), the calibration graph of the CL intensity versus vanillin concentration was linear range from 3.3×10^{-7} mol/L to 1.2×10^{-5} mol/L, and the detection limit was 1.1×10^{-7} mol/L (3δ). The regression equation shown in Fig. 8 (F) was $\Delta I = 3.0\ c + 2.9 \times 10^2$ (c being the vanillin concentration: 10^{-8} mol/L) with a correlation coefficient of 0.9980. A complete analysis, including all procedures were performed with a relative standard deviation of 3.9% for vanillin 5.0×10^{-7} mol/L in the sample ($n = 11$).

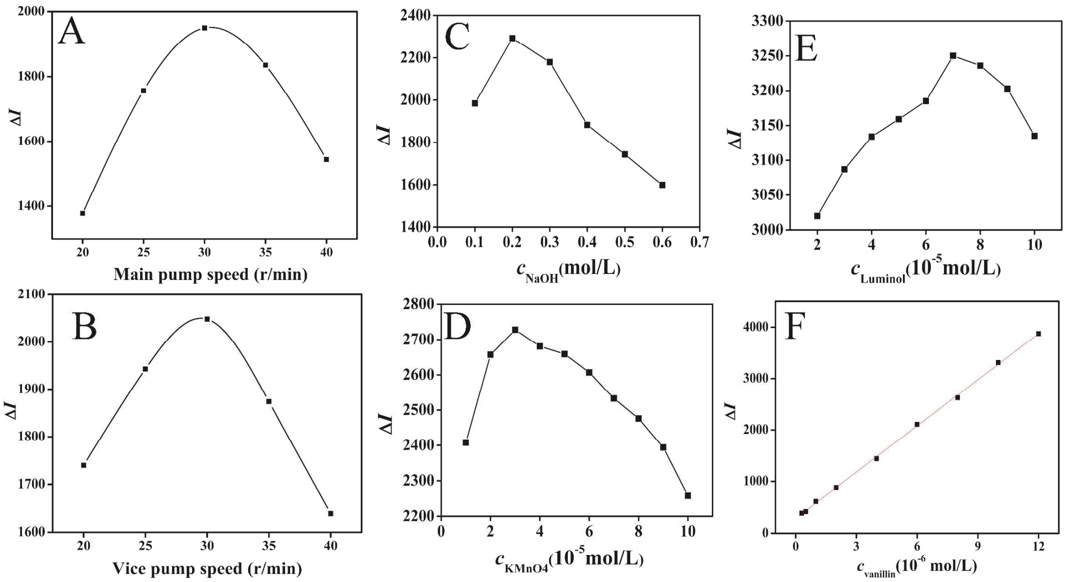


Fig. 8. Optimization results and regression equation. (C) Effect of NaOH concentration on CL intensity. Conditions: $c(KMnO_4) = 1.0 \times 10^{-4}$ mo/L, c(luminol) = 1.0×10^{-4} mol/L. (D) Effect of $KMnO_4$ concentration on CL intensity. Conditions: c(NaOH) = 0.2 mol/L, c(luminol) = 1.0×10^{-4} mo/L. (E) Effect of luminol concentration on CL intensity. Conditions: $c(KMnO_4) = 3.0 \times 10^{-5}$ mol/L, c(NaOH) = 0.2 mol/L. (F) Regression equation CL conditions: $c(KMnO_4) = 3.0 \times 10^{-5}$ mol/L, c(NaOH) = 0.2 mol/L, c(luminol) = 7.0×10^{-5} mo/L.

3.5 Interferences study

In order to apply the sensor to the analysis of abused vanillin in the practical samples, the interferences of some substances coexisted in the standard solution (1.0×10^{-6} mol/L vanillin) was examined under the optimal conditions The tolerable limits of coexisted species were taken as a relative error not larger than 5%. The results were shown in Fig. 9. Because of the similar structure, citric acid and salicylic acid had greater effects on the CL value, the interferences resulted from the non-special binding would be eliminated for detection of vanillin. All interference studies showed that the GM-MIP could be used as pretreatment material and improve sensitivity and selectivity of the flow injection CL sensor to the detection of vanillin.

3.6. The reusability of GM-MIP sensor

The adsorption capacity of GM-MIP to vanillin before and after use could be used to evaluate the reusability of the GM-MIP-CL sensor. The vanillin in used GM-MIP was extracted with methanol/acetic acid (9/1, *V*/*V*) by refluxing 24 h. According to the experiments, the used GM-MIP adsorption capacity could be gotten and then compared with the adsorption capacity of GM-MIP before any use. The result showed that 0.47×10^{-5} mol/g was tolerable to the concentration of 5.0×10^{-6} mol/L vanillin in 5 times which demonstrated that the sensor was reusable.

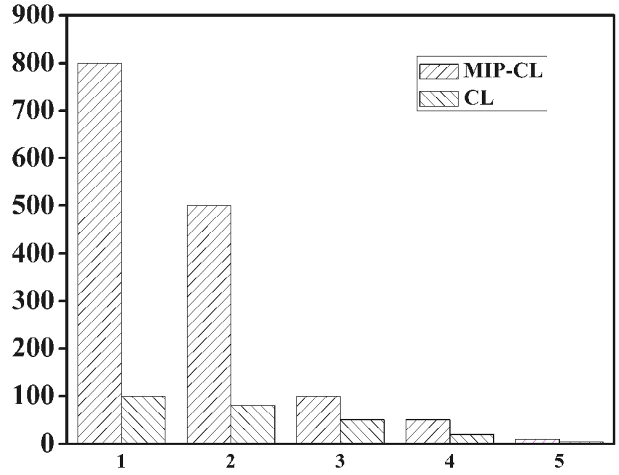


Fig. 9. Interferences study (Times). 1: K^+, Cl^-, Na^+, saccharose; 2: Zn^{2+}, Mg^{2+}, Fe^{3+}, BPA; 3: Sulfapyridine, -cyclodextrins, Amylaceum; 4: Citric acid; 5: Salicylic acid.

3.7 Application of the GM-MIP-CL sensor

Under the optimal experimental conditions, vanilla slice, vanilla milk tea and vanilla drink were analyzed respectively using molecularly imprinted CL sensors. Simple processing mode of samples were as follows: a grain of vanilla slice were taken, pulverizated and blended in the mortar, dissolved，shaked，filtered and constanted volume to 100.0 mL in volumetric flask. Vanilla milk tea and drinks were each taken 1.00 mL and diluted to 100.0 mL. The solutions were diluted step by step. According to the experimental method for determination of vanillin in solution, the analysis results were shown in Tab. 1.

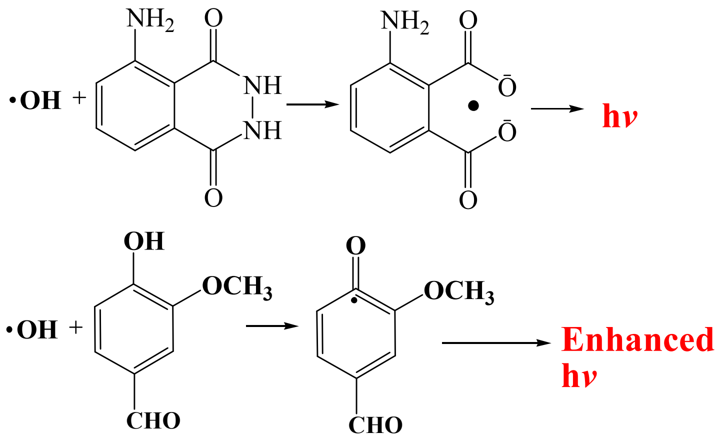
Tab. 1. Application of the sensor

Sample	*c* /10^{-6}mol/L (n=6)	RSD%	Added/10^{-6}mol/L	Found/10^{-6}mol/L	Recovery
Vanilla slice	0.63	2.9	0.5	1.10	94%
Vanilla tea	2.5	2.7	0.5	2.97	94%
Vanilla drink	5.0	3.4	0.5	5.44	88%

4 Conclusions

In this work, the vanillin-GM-MIP was synthesized by precipitation polymerization and used as molecule recognition material in the CL analysis. GO, GM, GM-MIP and GM-NIP were characterized by SEM, FTIR, XRD and TEM. The adsorption ability, selectivity and reusability of GM-MIP were also researched. Meanwhile, the GM-MIP column was placed in front of the pump with wet packing column to get an easy, simple and automatical column packing in CL analysis. The experimental conditions were also optimized. Based on this, the sensor was applied to determine the vanillin in the practical samples successfully and the results were very satisfactory. The possible mechanism was that luminol was oxidized by H_2O_2, reaseaing CL, while the vanillin was oxidized by H_2O_2 too, reaseaing CL, which would enhance CL intensity described in following equations.

$$H_2O_2 \longrightarrow \bullet OH$$



The obtained GM-MIP-CL sensor has shown to be a good potential for its real sample application with high selectivity, simple instrument and fast method for on-site determination of vanillin.

Acknowledgements

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