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CdTe quantum dots@luminol for trace-level chemiluminiscence sensing phenacetin based on biological recognition materials

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Abstract

A trace-level chemiluminiscence (CL) sensor for determination of phenacetin with CdTe quantum dots@luminol (QDs@luminol) as signal amplification based on chitosan/magnetic graphene oxide-molecularly imprinted polymer (CsMG-MIP) as biological recognition materials was fabricated. CdTe QDs@luminol, which was used in the preparing process of the sensor, could amplify the signal of CL based on chemiluminescence resonance energy transfer (CRET) with saving luminol. The CsMG-MIP, taking full advantage of abundant hydroxyl and amino in chitosan which could provide a lot of sites to form hydrogen bond in SMIP, using graphene oxide to improve adsorption capacity and Fe_3O_4 nanoparticles to make the preparation of recognition unit simple and easy, was introduced into CL. Under the optimized conditions of CL, phenacetin could be assayed in the range of 3.0×10^{-9} - 3.0×10^{-7} mol/L with a detection limit of 8.2×10^{-10} mol/L (3δ). With the advantages of amplifying the CL signal based on CRET and saving the consumption of luminol simultaneously, the sensor was successfully applied in determination of trace-level phenacetin in real samples with high selectivity and reagent economized way.

Keywords: phenacetin; chemiluminescence resonance energy transfer; graphene oxide; Fe_3O_4; molecularly imprinted polymer; CdTe quantum dots@luminol

1. Introduction

As it could cause methemoglobinemia, renal failure and even cancer for large dose or used for a long time, phenacetin has been withdrawn from the market in many countries [1,2]. In china et al., though it had strict requirements on dosage, phenacetin was not completely banned. Thus, the accurate control of phenacetin content in tablet was very important. Up to now, reported methods for the determination of phenacetin were electrochemical sensor [3], high performance liquid chromatography [4], biomimic bulk acoustic wave method [5] and spectrophotometric method [6]. Nevertheless, these methods were more or less limited by complicated processes, expensive equipment or high cost during the procedures. Hence, development of a higher efficient method for the detection of phenacetin was of important significance. With the advantages of high sensitivity, simple instrument, no interference from background scattering light, chemiluminescence (CL) technique has been developed to be a powerful tool over the past several decades in various fields [7]. And CL of CdTe nanocrystals have been researched several years ago [8, 9].

In nanoscale space, with properties positively changed following the structurally diameter changed, Quantum dots (QDs) were the important part of nanometre science and technology [10]. Due to their unique optical and physical properties such as high photo stability, broad adsorption spectra and narrow emission range, QDs had attracted much attention and had been used in *in vivo* imaging [11], fluorescence probe [12] and biological luminescent labels [13] etc. With the booming research of QDs, QDs compound was also an exciting direction in nanoscience fields of the current century [14]. CdTe QDs@luminol conjugates, a modification of the surface of QDs with luminol, could proceed with intermolecular resonance energy transfer between chemiluminescence donor luminol and receptor QDs [15]. For the surface changes of QDs, their properties in particular the CRET process changed accordingly

[16, 17]. It was found that CdTe QDs@luminol was to be a potential material that could amplify CL single with higher CRET efficiency [15].

Chemiluminescence resonance energy transfer (CRET) has been applied in the detection domain by using intra and intermolecular energy transfer process since put forward [18]. The advantages of CRET were that none fluorescent light source which could minimize nonspecific signal caused by external light excitation often observed in fluorescence-based measurement was necessary [19]. CRET was a widely applied technique for its dramatically reducing the fluorescence bleaching and lessening the autofluorescence of the system.

At present, as biological recognition materials, molecular imprinting polymer (MIP) has been developed to be mature since pioneered by Wulff G [20] in the early 1970s and has been applied in many fields [21]. In recent years, basically because of its high specific surface area, unique thermal, and mechanical properties, graphene oxide (GO) has attracted considerable attention [22, 23] and widely used many fields [24]. For its high specific surface area, GO could be used as supporting plane in synthesizing new material just like what we done in this paper. Magnetic graphene oxide (MG) had attracted great attention in various application areas [25]. The advantages of chitosan/magnetic graphene oxide (CsMG) such as easy separation, stable physical properties, low toxicity and eco-friendliness were performed incisively and vividly.

In this work, based on intramolecular CRET in CdTe QDs@luminol, a trace-level CL sensor with CsMG-MIP as biological recognition materials for phenacetin determination was established. In the CdTe QDs@luminol-CsMG-MIP CL sensor, CdTe QDs@luminol could not only amplify the single of CL greatly based on CRET but also save the consumption of luminol, CsMG-MIP, taking full

advantage of abundant hydroxyl and amino in chitosan which could provide a lot of sites to form hydrogen bond in SMIP, using graphene oxide to improve adsorption capacity and Fe_3O_4 nanoparticles to make the preparation of recognition unit simple and easy, could improve selectivity with making the preparation process simple. Under the chosen conditions of CL, the CdTe QDs@luminol-CsMG-MIP-CL sensor was applied in detection of phenacetin in real samples, and the sensor showed high sensitivity and selectivity.

2 Experimental

2.1 Chemicals and materials

Phenacetin (98%) and Ethylene glycol dimethacrylate (EGDMA, A.R) was supplied by Aladdin Industrial Co. (China); Acrylamide (A.R), $CdCl_2 \cdot 2H_2O$ (A.R), 2,2-azobisisobutyronitrile (AIBN, A.R), Sodium thioglycolate (80%) and KBH_4 (96%) were purchased from Sinopharm Chemical Reagent Co. Ltd (China); The ethanol, acetic acid, potassium hydroxide, methanol, luminol and all the other chemicals unless specified were of analytical reagent grade and used without further purification unless specified.

EGDMA was distilled under operation pressure to remove inhibitors and AIBN was recrystallised with methanol prior to its first use. Redistilled water was used throughout the work.

2.2 The CdTe QDs@luminol-CsMG-MIP CL sensor

The IFFM-E flow injection CL analyzer (Xi'an Remex Electronic instrument High-Tech Ltd., China) was equipped with an automatic injection system and a detection system. PTFE tubes (id. 0.8 mm) were used to connect all the components in the flow system. Glass capillary filling with CdTe QDs@luminol was positioned on the CL detection window. A certain amount CsMG-MIP (CsMG-NIP) was placed

in front of the CL analyser as recognition elements. The CL signal was recorded by a computer and the data was disposed by software. The mechanism of sensor used in this work was shown in Fig. 1(A).

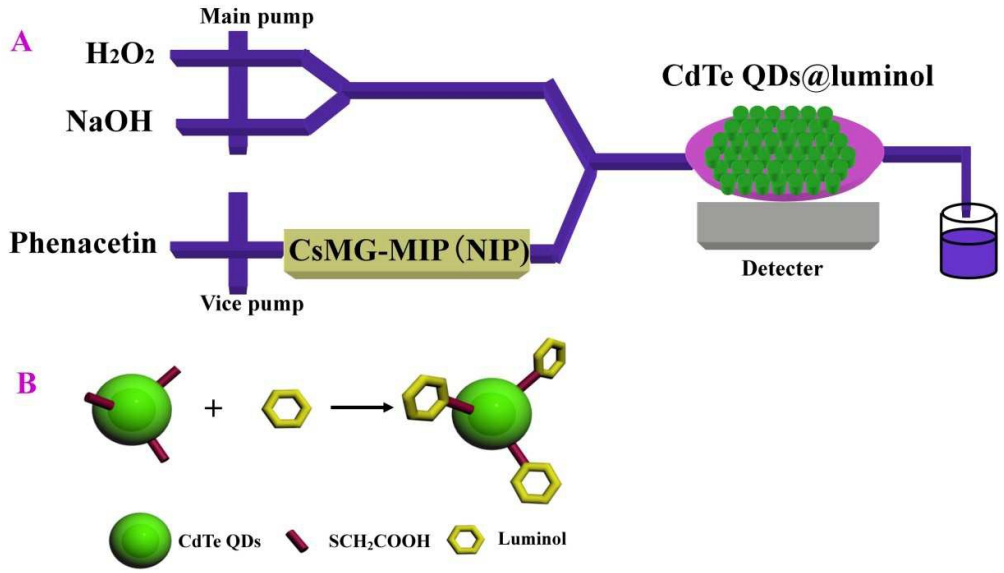

Fig.1. The mechanism of CL sensor (A) and the preparation process of CdTe QDs@luminol (B)

2.3 Preparation of CdTe QDs@luminol

Thioglycolic acid capped CdTe QDs and CdTe QDs@ luminol were synthesized according to a modified procedure described in the previous literatures [15]. The preparation process of CdTe QDs@luminol was shown in Fig. 1 (B).

Firstly, NaHTe solution was added to N_2-saturated 0.1142 g $CdCl_2 \cdot 2H_2O$ solution in the presence of sodium thioglycolate and degassed with N_2. Then, the pH of the solution was adjusted to 9.5. The reaction solution was heated and refluxed to prepare thioglycolic acid-capped CdTe QDs. Luminol was conjugated to thioglycolic acid-capped CdTe QDs using EGDMA as a coupling reagent. CdTe QDs were added into 1.0 mL of luminol-H_3BO_3-KOH buffer solution containing 0.01g of EGDMA. Then, the mixture was stirred for 2 h. Finally, the prepared solutions were purified by precipitating with methanol. The final product was dried in an oven for use.

2.4 Preparation of CsMG-MIP and CsMG-NIP

Graphene oxide was prepared from nature graphite powders by a modified Hummers method [26] and our previous work [27]. 5.0 g graphite powder were added into a 500 mL flask ontaining180 mL H_2SO_4 and 20 mL HNO_3 and then cooled. After being well dispersed, 15 g $KMnO_4$ was added under stirring. When the color turned into brownish, 150 mL of H_2O_2 was slowly added to the paste with agitation. Then, the mixture was washed until the pH = 7 while ultrasonication and dried to get GO.

CsMG was prepared according to the previous literature [28] and the methods of our previous work [27], respectively. By suspending 0.2 g chitosan in 40 mL of 2% acetic acid by ultrasonication, 0.1 g magnetic particles and 0.1 g GO were added to the molten chitosan while stirring. Then, 6 mL glutaraldehyde was added to the mixed solution. Then, sodium hydroxide was added till the pH=10.5. The reaction was carried out and the precipitate was isolated in the magnetic field, washed and dried.

Preparation of the phenacetin-CsMG-MIP and phenacetin-CsMG-NIP was carried out according to reports [29]. 0.8 mmol methacrylic acid and 0.2 mmol phenacetin were dispersed into 30 mL ethanol. After shaking, 0.05 g CsMG, 8.0 mmol EGDMA and 30 mg AIBN was added under nitrogen protection at 65 °C. Then, the mixture was shaked for 8 h. The obtained product was washedand dried. The CsMG-NIP was prepared in the same way but without any phenacetin.

2.5 Adsorption performance of CsMG-MIP and CsMG-NIP

The adsorption capacity of CsMG-MIP and CsMG-NIP for phenacetin was investigated as follows: 20.0 mg of CsMG-MIP (CsMG-NIP) was mixed up with 10.0 mL of phenacetin solution (1.0×10^{-2} mol/L) in a 50 mL iodine flask and oscillated 24 h for adsorption.

3 Results and discussion

CdTe QDs@luminol as signal amplification based on CRET and CsMG-MIP as biological recognition materials were synthesized in developing a CL sensor for trace-level determination of phenacetin.

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

The SEM was used to characterize the surface morphology of the GO (a), CsMG (b), CsMG-MIP (c) and CsMG-NIP (d), and the SEM images were shown in Fig. 2. As it could be observed in Fig. 2 (a), the image showed that the prepared GO presented the sheet-like structure with small thickness, smooth surface, and wrinkled edge. The folding nature was clearly visible. As it shown in Fig. 2 (b), the Fe_3O_4 spheres were uniformly decorated and anchored on the wrinkled GO layers with a high density. Hence, we considered that the Fe_3O_4 NPs were stably attached to the GO surface which could served as a stabilizer against the aggregation of GO and enable the separation of the products easy.

The SEM images of CsMG-MIP and CsMG-NIP were showed in Fig. 2 (c) (d) respectively. As we could see, the surface of synthesized CsMG-MIP was rough while the surface of CsMG-NIP was very smooth. The cavities on the CsMG-MIP were suitable for the recognition of phenacetin. The obvious difference between CsMG-MIP and CsMG-NIP indicated the successful synthesis of imprinting cavities on the surface of CsMG-MIP.

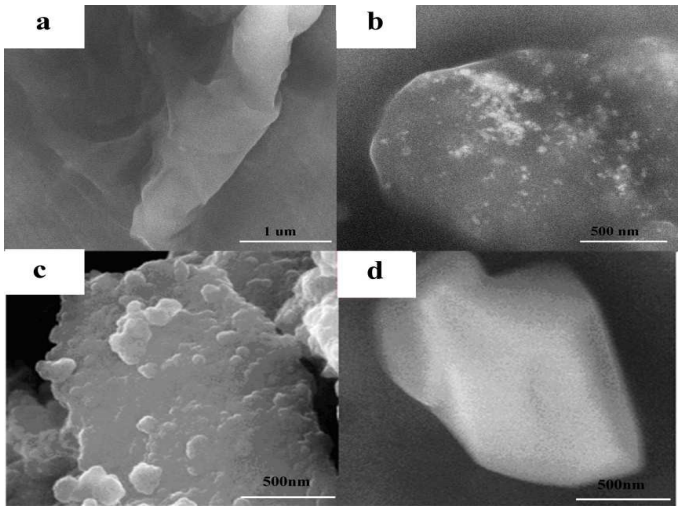

Fig.2. The SEM images of GO (a), CsMG (b), CsMG-MIP (c) and CsMG-NIP (d)

3.2 Characterization of CdTe QDs and CdTe QDs@luminol

The FTIR spectrum of the CdTe QDs and CdTe QDs@luminol particles were recorded within the range of 4000 - 500 cm^{-1}, and shown in Fig. 3 (a). The peak at 670 cm^{-1} is the stretching vibration of C-S. It could be seen that the stretching vibration of secondary amine contributed to the strong adsorption at 3350 cm^{-1}. In the spectra of CdTe QDs@luminol, peaks at around 1108 and 1680 cm^{-1} were due to the bending and stretching vibration of C=O respectively, which provided evidence of the successful preparation of CdTe QDs@luminol.

As we could see in Fig. 3 (b), the first adsorption peak of CdTe QDs was located at about 530 nm and a symmetric emission peak was located at about 560 nm. The relatively narrow emission peak was a signature of a narrow distribution of QDs diameters.

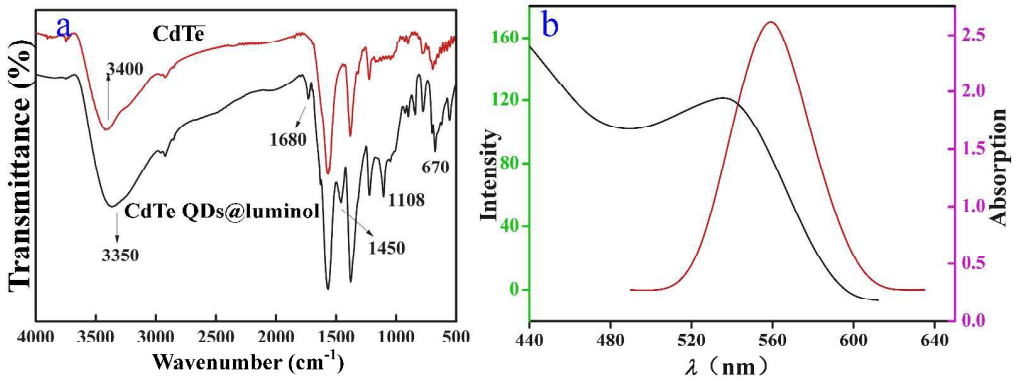

Fig.3. The FTIR spectra of CdTe QDs and CdTe QDs@luminol (a); the adsorption (red line) and emission (green line) spectra of CdTe QDs (b)

3.3 Adsorption capacity of CsMG-MIP and CsMG-NIP

The amount of phenacetin absorbed by the CsMG-MIP determined the adsorption capacity which not only influenced the detection limit but also the selectivity of the method. The adsorption capacity (Q) was calculated by the following formula:

$$Q = \frac{V}{m}(c_0 - c_e)$$

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

The Q of phenacetin on the maximum adsorptions of CsMG-MIP and CsMG-NIP were 12.3×10^{-5} mol/g and 1.6×10^{-5} mol/g. Because of complementary spatial structure imprinted cavities on the surface of CsMG-MIP, the target molecules could be adsorbed highly and rapidly by CsMG-MIP. But in contrast, poor adsorption capacity of CsMG-NIP was obtained for the absence of imprinting cavities. The results demonstrated that the CsMG-MIP was suitable for use in CL sensor.

3.4 CL reaction conditions

The concentrations of H_2O_2 and NaOH had great effects on the CL reaction. So, the optimal concentration conditions were 1.0×10^{-5} mol/ L of NaOH and 0.2 mol/L of H_2O_2, respectively, as shown in Fig.4 (a) (b).

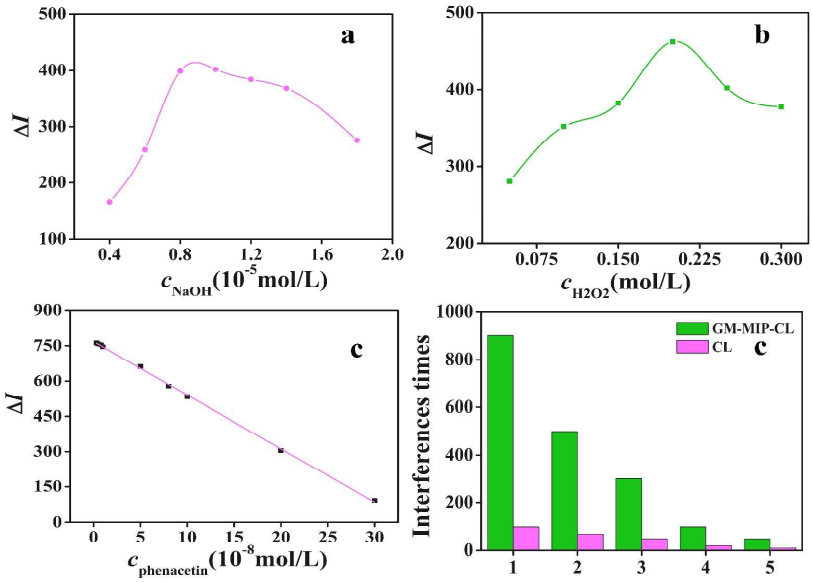

Fig.4. Optimization results and interferences study. (a) Effect of NaOH concentration on CL intensity. Conditions: $c(H_2O_2)$ = 0.1 mol/L. (b) Effect of H_2O_2 concentration on CL intensity. Conditions: c(NaOH) = 1.0×10^{-5} mol/L. (c) The regression equation. (d) Interferences study of CsMG-MIP-CL sensor. 1. Na^+, K^+, Mg^{2+}, 2. Sugar, Glucose, 3. Sodium citrate, 4. Aminopyrine, 5. Epinephrine, Paracetamol.

3.5 Analytical performance of CdTe QDs@luminol-CsMG-MIP-CL sensor

Under the optimum conditions ($c(H_2O_2)$ = 0.2 mol/L, c(NaOH) = 1.0×10^{-5} mol/L, the required amount of CdTe QDs@luminol), the analytical performance of the proposed CdTe QDs@luminol-CsMG-MIP-CL sensor was studied. The calibrations was linear in the range of 3.0×10^{-9} - 3.0×10^{-7} mol/L and was described by the calibration curve $\Delta I = 769 - 2.3 \times 10^9\ c$ (mol/L, $R^2 = 0.9992$) shown in Fig. 4 (c). The RSD was 2.9% (n = 11) by determination of 1.0×10^{-8} mol/L phenacetin, and the detection limit was 8.2×10^{-10} mol/L (3δ), which was compared with

conventional methods, and the results were shown in Table 1. The CL sensor, which using CdTe QDs@luminol as CL single amplifier and CsMG-MIP as recognition material, exhibited low detection limit, high sensitivity and selectivity.

Tab.1. Comparing results with conventional methods

Method	Linear range (nmol/L)	Detection limit (nmol/L)
Our work	$3.0 - 3.0\times10^{2}$	0.82
Electrochemical sensor [3]	$60 - 1.0\times10^{4}$	
High performance liquid chromatography [4]	$1.1\times10^{2} - 1.1\times10^{4}$	1.1×10^{2}
Biomimic bulk acoustic wave method [5]	$50 - 5.0\times10^{5}$	5.0
Spectrophotometric method [6]	$1.1\times10^{4} - 1.3\times10^{5}$	

3.6 Interferences study on CdTe QDs@luminol-CsMG-MIP-CL sensor

Some chemical active compounds in samples can also be oxidized under the same conditions. The interferences caused by these compounds were researched in detail. As shown in Fig. 4 (d), the tolerable limits of coexisted species were taken as a relative error not larger than 5% in the standard solution of phenacetin with the concentration of 1.0×10^{-8} mol/L. The interferences from aminopyrine, paracetamol and epinephrine were very serious because their spatial structures were similar to phenacetin. To the critical, these compounds usually coexisted in real samples. Conversely, they could only have small interferences when using CsMG-MIP for the imprinting cavities on the surface of CsMG-MIP which could recognize and adsorb phenacetin specially and could not recognize and adsorb aminopyrine, paracetamol and epinephrine, which made small interferences be observed from aminopyrine, paracetamol and epinephrine when using CsMG-MIP. The above evidence gave persuasive evidence that CsMG-MIP could be used as pretreatment material to improve selectivity of the CL sensor.

3.7 Application of the CdTe QDs@luminol-CsMG-MIP CL sensor

To assess the performance of the proposed sensor for real pharmaceutical applications, samples were obtained from Qutong tablet and Children keganmin powder for analysis. And in order to research the application of the sensor in complicated biological samples, matrix samples containing dyes, some biomacromolecule and food additives were mixed up with the waste water from our laboratory. Under the optimal experimental conditions, the analytical results were shown in Tab. 2, and it demonstrated that the CdTe QDs@luminol-CsMG-MIP CL sensor used for the determination of phenacetin was practical.

Tab.2. Application of sensor

Sample	c /10^{-8} mol/L (n=6)	RSD%	Added/10^{-8} mol/L	Found (n=6)	Recovery%
Qutong tablet	3.3	3.2	3.0	6.0	91
			5.0	8.1	94
Children keganmin powder	5.7	3.7	3.0	8.8	102
			5.0	10.4	95
Complicated biological samples	5.1	3.7	3.0	7.8	90
			5.0	9.5	88

3.8 The possible CL mechanism

Thioglycolic acid capped CdTe QDs chemically modified by luminol were used as signal amplifier based on intramolecular CRET in CdTe QDs@luminol to determine phenacetin with CsMG-MIP CL sensor. The first use of CdTe QDs@luminol into analytical domain was a great success. The possible CL mechanism was shown in Fig. 5. At the beginning, the back of the oxidized-state

luminol to the ground state would emit photons, producing 'hν_1'. Then, the intramolecular CRET in the CdTe QDs@luminol conjugate, which was due to the overlapping areas between the emission spectrum of luminol and adsorption spectrum of CdTe QDs, could amplify the CL intensity which occured by using luminol-H_2O_2 system as energy donor and CdTe QDs as acceptor. And high-energy CdTe QDs returned to ground state with photon emission, producing 'hν_2'. For the existing of luminol in the CL system, the mechanism could be that either CdTe QDs were the final emitter due to CRET, or a catalytic when the final emitter was the excited-state phenacetin. It was also possible that the direct oxidation of CdTe QDs and CRET process took place simultaneously. On the other hand, for the excited-state phenacetin which was oxidized by H_2O_2 full of energy returning to the ground state, 'hν_3' intensity was enhanced and it showed the CL signal increased with the increase of phenacetin correspondingly. In conclusion, the detected signal was the CL of luminol, the fluorescence of CdTe QDs excited by the CL of luminal and the CL of phenacetin. This route has clearly indicated that CdTe QDs@luminol were remarkably effective on the detection of phenacetin.

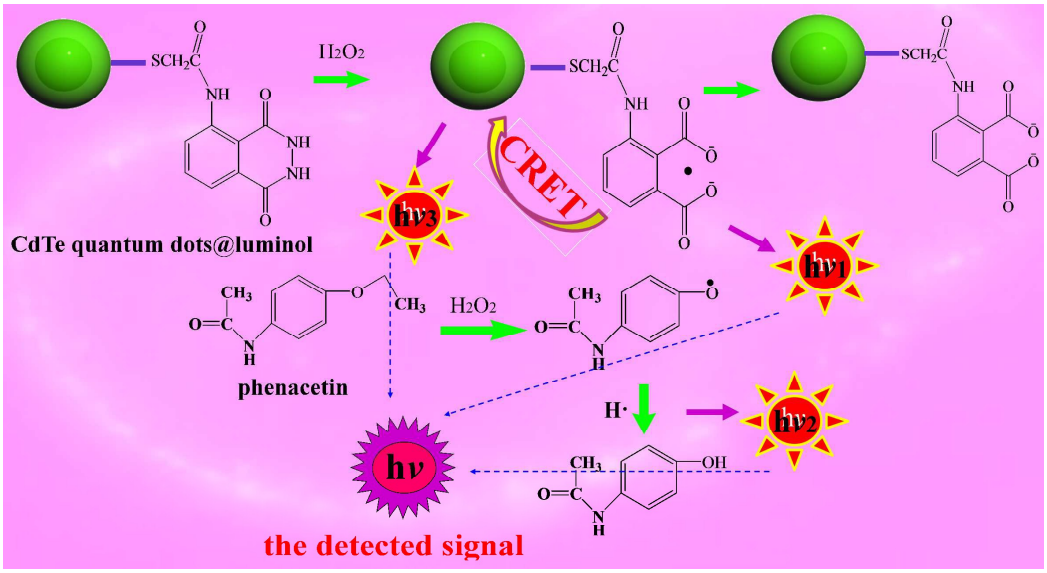

Fig.5. The possible chemiluminescence mechanism

4 Conclusion

Firstly, thioglycolic acid capped CdTe QDs chemically modified by luminol and biological recognition materials chitosan/magnetic graphene oxide-molecularly imprinted polymer were synthesized. Secondly, the adsorption capacity of chitosan/magnetic graphene oxide-molecularly imprinted polymer was studied to be 12.3×10^{-5} mol/g. Thirdly, the effects of luminous reagents' concentrations on Chemiluminescence were explored. Fourthly, the regression curve, liner range, detection limit and interference were investigated. The detection limit was 8.2×10^{-10} mol/L (3δ) which was lower than traditional methods. Finally, the interference and reusability of chitosan/magnetic graphene oxide-molecularly imprinted polymer was discussed. It was found that the proposed trace-level sensor was able to extraordinarily analysis phenacetin in complex samples with high sensitivity, selectivity and reagent economized way.

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CL signal was amplified by CRET in CdTe QDs@luminol to improve sensitivity and CsMG-MIP was introduced to improve selectivity