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Gold nanoclusters-enhanced peroxynitrous acid chemiluminescence for high selectivity sensing of nitrite

Yanyan Sui[a], Mao Deng[b], Shuangjiao Xu[a] and Funan Chen[a,*]

[a]The Key Laboratory of Luminescence and Real-time Analytical chemistry, Ministry of Education; School of Chemistry and Chemical Engineering, Southwest University, Chongqing, China 400715

[b]Qianjiang Environmental Monitoring Centre, Chongqing, China

Contact information for Corresponding Author

Associate Professor Funan Chen, School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, P.R. China

Fax: 86-23-68258363. Tel: +86-18883255598

E-mail: chenfn@swu.edu.cn

Abstract:

Peroxynitrous acid (ONOOH) produced by online mixing of nitrite and acidified hydrogen peroxide could induce weak chemiluminescence (CL). A stronger chemiluminescence was observed in the presence of gold nanoclusters (Au NCs). This novel CL system was developed as a flow-injection method for the nitrite determination directly and conveniently. This method was achieved in acidic medium, which greatly improve its selectivity. The CL mechanism of the peroxynitrous acid-gold nanoclusters system was investigated using the CL spectra, UV-visible spectroscopy and radical scavengers. The enhanced CL could be attributed to the catalysis of Au nanoclusters. The proposed method has been applied to determine nitrite in water samples with good accuracy and precision.

Keywords:

Gold nanoclusters; flow-injection; chemiluminescence; peroxynitrous acid; nitrite.

1. Introduction

Nitrite, as a characteristic pollutant and fertilizing agent for food, is widely present in the environment [1, 2]. The reaction of nitrite with secondary amines could form carcinogenic N-nitrosamines, which is extremely harmful to humankind [3]. Thus, the concentration of nitrite in water environment is one of the most important indicators of water quality. It is also reported that nitrite has caused serious hazards to the nervous system, spleen and kidneys. Therefore, it is of great importance to detect nitrite quantitatively in water sources.

Due to the harmness of nitrite to environment and human health, a lot of analytical methods based on different principles have been developed for the determination of nitrite, such as UV-vis absorbance[4,5], electrochemistry[6,7], chemiluminescence (CL) [8-10,15-20] and fluorometric approaches[11-13]. The conventional UV-vis absorbance methods for determinatng nitrite are usually based on the diazo coupling reaction [4, 5]. In order to obtain high sensitivity and selectivity, the long coupling process requires exquisite control of pH and temperature. The electrochemical process always needs complex electrodes [6, 7]. Fluorescent dyes are necessary for the fluorescent detection, which need to react with nitrite in this process, thus may cause potential strong background fluorescence in the real samples [13].

Chemiluminescence, as a sensitive, facile, and rapid analytical method, has been well applied to the detection of nitrite in environmental monitoring and food safety. The gas phase CL assays for nitrite [8, 14] are based on the reduction of nitrite to nitric oxide (NO), which could react with ozone to produce CL signal. However, such transformation suffers from complicated procedure. In the aqueous phase [15], the detection of nitrite is based on

that nitrite can react with acidified hydrogen peroxide to form unstable peroxynitrous acid (ONOOH), which can be quenched to peroxynitrite by an alkaline reagent. The decomposition of peroxynitrite with weak CL signal has been developed as a flow-injection method for nitrite sensing [16]. Mikuska et al. [17] reported peroxynitrous acid (ONOOH) can react with alkaline luminol and built a CL method for the nitrite detection. The weak CL from excited peroxynitrous acid also could be amplified by energy acceptors, such as uranine [16], CdTe quantum dots [18], Fluorosurfactant (FSN)-gold nanoparticles [19]. These methods were interfered with some transition metals, because they were achieved in alkaline media. In order to improve the selectivity, cation-exchange column was introduced, which may make the detection more complex. Therefore, it is an attractive research area to develop more simple and convenient ONOOH/$ONOO^-$ CL reactions in acidic system.

As a new class of metal nanostructures, metal nanoclusters (NCs) have attracted great attention due to their unique properties and versatile applications [20-26]. Among the metal nanoclusters, Au nanoclusters (Au NCs) exhibit fascinating features, including facile synthesis, good water solubility, low toxicity, and long term stability. Because of these attractive features, gold nanoclusters have attracted significant research efforts recently. Until now, the application of Au NCs in analytical fields mainly focused on their fluorescence properties. It would be interesting to find that AuNCs have effect on peroxide induced ultra-weak CL reactions. In this work, we found that the weak CL emission from the reaction of nitrite with hydrogen peroxide in acidic medium was greatly enhanced by Au NCs. And the CL intensity was proportional to the concentration of nitrite, which led to a novel sensing platform based on the activities of Au NCs in direct nitrite determination.

The proposed method was achieved in acidic medium, which greatly improve its selectivity. This method can be used to detect trace nitrite in tap water, river water and pond water with acceptable selectivity and reproducibility. This work is an example of the successful analytical application of nanoparticles-enhanced CL.

2. Experimental

2.1Reagents and materials.

All chemical reagents were of analytical grade and used without further purification. And ultrapure water was used throughout. Sodium nitrite was obtained from Chongqing Beibei Chemical Reagent Co. Ltd. (Chongqing, China). $HAuCl_4 \cdot 3H_2O$ was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Bovine serum albumin (BSA) was supplied by Sangon Biotech Co. Ltd. (Shanghai, China). Hydrogen peroxide (H_2O_2, 30%), sodium hydroxide, Sulfuric acid (98%) and nitro blue tetrazolium (NBT) were purchased from Kelong Reagent Co. Ltd. (Chengdu, China). Thiourea and ascorbic acid (AA) were commercially obtained from Chongqing Chemical Regent Company (Chongqing, China).

2.2 Synthesis of BSA-Au nanoclusters.

BSA stablilized Au NCs were synthesized in aqueous solution according to the previously reported method [27]. In a typical experiment, all the glassware were thoroughly cleaned with aqua regia (V_{HNO_3}: V_{HCl}, 1:3) and rinsed extensively with double distilled water prior to use. Aqueous $HAuCl_4$ solution (5 mL, 10 mM, 37 ℃) was added

to BSA solution (5 mL, 50 mg/mL, 37 ℃) under vigorous stirring. Two minutes later, an aqueous solution of NaOH (0.5 mL, 1 M) was introduced, and the mixture was incubated at 37 ℃ for 24 h under vigorous stirring. The color of the solution changed from light yellow to light brown, and then to deep brown.The solution was then dialyzed in ultra-pure water for 24 h to remove unreacted BSA. The final solution was stored at 4℃ in refrigerator when not in use.

2.3 Sample preparation.

Tap water was analyzed without any pretreatment. River water and pond water were filtered through a membrane filter of 0.22-μm pore size and spiked with 1.0×10^{-5} M EDTA as a masking reagent for transition metal before the CL determination.

2.4 General procedure for CL analysis.

The FI system, as shown in Fig.1, was carried out on a laboratory-built flow injection CL system（Xi'an Remax Company, Xi'an, China）. The flow-injection system was consisted of two peristaltic pumps to deliver the reactants to the flow cell. One delivered water (Water was used as the carrier for nitrite and sample.) with one channel at a flow rate (per tube) of 2.0 mL/min. The other pump was used to carry H_2O_2 and Au NCs solution with two channels at the same flow rate. The PTFE tubing (0.8 mm i.d.) was used to connect all components in the flow system. A six-way injection valve equipped with an 8 cm long sampling loop was used to inject. The CL signal was detected by a photomultiplier tube (operated at −1k V), and then recorded by a computer equipped with

a data acquisition interface. Data acquisition and treatment were performed with BPCL software running under Windows XP. Determination of nitrites was performed based on the net CL intensity of $\Delta I = I_0 - I_s$, where I_0 and I_s denote the CL intensity in the absence and presence of nitrites, respectively.

3. Results and discussion

3.1 CL from Au NCs-$NaNO_2$-H_2O_2 system.

ONOOH, as a small inorganic nitrogen-containing hydroperoxide, is a strong acid. A method for preparation of ONOOH is the reaction of $NaNO_2$ with H_2O_2 in acid medium [28]. In this work, ONOOH was formed by the online mixing of $NaNO_2$ and acidified H_2O_2 (Reaction 1) [39-30]. Then, light emission was caused from the transform of ONOOH to nitrite via the stage of $HOONO^*$ (Reaction 2) [32-33].

$$HNO_2 + H_2O_2 \longrightarrow ONOOH + H_2O \qquad (1)$$

$$ONOOH \longrightarrow ONOOH^* + NO_3^- \qquad (2)$$

The ultra-weak CL emission resulting from the reaction of $NaNO_2$ and acidified H_2O_2 was recorded in Fig.2 (A) curve 1. However, the interaction mentioned was accompanied by a strong CL signal in the presence of Au NCs (curve 2). From it, we can see the CL signal intensity was enhanced about 20 times when the Au NCs was introduced. As shown in Fig.2 (B), the reaction between Au NCs and H_2O_2 brought a weak CL enhancement in comparison of two CL signal curves, which indicated that the contribution of H_2O_2 to the high CL intensity could not be ignored. From the above CL signals, we believe that the

154 system of Au NCs-$NaNO_2$-H_2O_2 can be developed as a flow-injection analysis for the
155 detection of nitrite.
156
157 *3.2 Optimization of the reaction conditions.*
158 To establish the optimal conditions for the analysis of nitrite, the effects of the
159 concentration of H_2SO_4, Au NCs, H_2O_2 and flow rate on the CL analysis were investigated
160 (Fig.3). It was found that no CL signal has been discovered in the absence of H_2SO_4,
161 because ONOOH only could be formed in an acidic medium. Therefore, the concentration
162 of H_2SO_4 was investigated in the range of 0.01-0.5 M (Fig.3A). With the increase of
163 concentration from 0.01 to 0.04 M, the CL intensity increased sharply and then decreased
164 obviously beyond 0.3 M. As a consequence, 0.04 M was selected as the optimum H_2SO_4
165 concentration in the present system.
166 The effect of H_2O_2 concentration on the CL was studied in the range from 0.01 to 0.05 M
167 (Fig. 3B), the CL intensity increased with the increasing H_2O_2 concentration in the range of
168 0.01 to 0.2 M and changed slowly beyond 0.3 M. Consequently, 0.2 M was chosen as the
169 optimal H_2O_2 concentration in the present study.
170 The flow rate was discussed as shown in Fig. 3D.We found that the CL signal increased
171 with the increasing flow rate. As we all know, a slower or more rapid flow rate could lead to
172 a CL reaction occurring before or behind the flow cell. Thus, 2.0 mL/min was chosen as the
173 most suitable flow rate. The effect of the concentration of Au NCs was also investigated in
174 the range of 2.0×10^{-6} to 6.0×10^{-5} M, and the optimal concentration was 8.0×10^{-6} M (Fig.3C).
175 In view of the CL intensity and the consumption of the regents, the optimized conditions

for CL system were as follows: 0.2 M H_2O_2 in H_2SO_4 solution (0.04 M), 8.0×10^{-6} M Au NCs, and the flow rate was 2.0 mL/min.

3.3 Mechanism Discussion.

The ultra-weak CL emission resulting from the reaction of $NaNO_2$ and acidified H_2O_2 was owing to the transform of ONOOH to nitrite via the stage of $HOONO^*$. It was found the effect of nanoparticles in a liquid-phase CL reaction could act as catalysts [31] or emitters [32]. A F-2500 mode fluorescence spectrophotometer with the xenon lamp turned off had been used to discuss the CL mechanism of $NaNO_2$-H_2O_2 system in the presence or absence of Au NCs. As shown in Fig.4, the CL spectrum for Au NCs-$NaNO_2$-H_2O_2 system located in the range of 360-400 nm and centered at 379 nm. While the light emission from the transform of ONOOH to nitrate via the HOONO* stage is believed in the wavelength region of 350-450 nm [33-34], which is in good agreement with the CL spectrum of Au NCs-$NaNO_2$-H_2O_2 system. Therefore, the adding of Au NCs did not generate a new luminophor in this CL system. The enhanced CL signal was thus attributed to the possible catalysis from Au NCs.

In order to further confirm the possible mechanism, the UV–visible absorption spectra were recorded. As shown in Fig. 5, the maximum absorption peak of $NaNO_2$ was observed at around 354 nm .The peak became lower with the addition of acidified H_2O_2 into $NaNO_2$ solution .This change could be attributed to the isomerization of ONOOH, which was formed by the mixing of $NaNO_2$ and acidified H_2O_2 (Reaction 2). No new absorption peak appeared when Au NCs were introduced into $NaNO_2$-H_2O_2 system. From the above all, the

198 enhancement of CL signal might be derived from the catalytic effect of Au NCs.

199 The mechanism was also confirmed by the quenching effect of different reactive oxygen
200 species (ROS) on the CL system. Singlet oxygen ($^1O_2$) as a CL emitter has been reported to
201 exist in the $NaNO_2$-H_2O_2 system (Reaction 3-5) [35]. Sodium azide (NaN_3), a well-known
202 quencher of singlet oxygen ($^1O_2$) [35, 36], was used in the present experiment. And the result
203 showed that 5 mM NaN_3 had no inhibition of the CL intensity, which provided strong
204 evidence that $^1O_2$ was not existing in the Au NCs-$NaNO_2$-H_2O_2 system. (Table.1)

205

206 $$ONOOH \rightleftharpoons \cdot NO_2 + \cdot OH \quad (3)$$

207 $$ONOOH + H_2O_2 \longrightarrow O_2^{\cdot -} + \cdot NO_2 + H^+ + H_2O \quad (4)$$

208 $$O_2^{\cdot -} + \cdot OH \longrightarrow {}^1O_2 + OH^- \quad (5)$$

209

210 Ascorbic acid (AA) is well known as an efficient ROS scavenger [37], it can terminate
211 active oxygen radicals by electron transfer. Ascorbic acid with a concentration of 1 mM had
212 a negative effect on the signal, which illustrated that the generation of free radicals
213 appeared to be important in the CL reaction. NBT is frequently used for the detection of
214 $O_2^{\cdot -}$ radicals, because it can reduce NBT to its deep blue diformazan form [38]. When 1mM
215 NBT was added to the CL system, the CL intensity decreased by a factor of ~60.0.
216 Thiourea is an effective radical scavenger for hydroxyl radical (OH·) [39]. When 5 mM
217 thiourea was added to the CL system, a distinct inhibition was observed by the factor of
218 ~61.1.The results evidently supported the assumption that $O_2^{\cdot -}$ and OH· was the
219 intermediate in the CL reaction. It was reported that H_2O_2 decomposition on supported

metal catalysts such as Au NPs, Ag NPs and CuO NPs involved the formation of hydroxyl radicals OH·. We suggested that the O–O bond of H_2O_2 might be broken up into double OH· radicals by virtue of the catalysis of Au nanoclusters. Then the OH· radicals reacted with $\cdot NO_2$ to form the ONOOH (Reaction 3), and then ONOOH was transformed to nitrate via the HOONO*, which cause the light emission. Based on the above results, the whole enhanced mechanism is summarized in Scheme.1.

3.4 Analytical performance.

Nitrite is widely present in the environment and is used as preservatives and fertilizing reagents for food. The possibility of proposed method to detect nitrite was studied (Fig. 6). Under the optimum conditions described above, there is a good linear relationship between CL intensity and the nitrite concentration in the range from 5uM to 0.1 mM with a correlation coefficient of 0.9991 and the regression equation is $\Delta I=24.05 + 48.46$ [Nitrite] (M). The limit of detection (LOD, 3σ) for nitrite was 4.7 uM. The relative standard deviation (RSD) for 9 repeated measurements of 0.8 uM nitrite was 2.3%.

3.5 Interference study.

The selectivity of the proposed method was evaluated by analyzing a standard solution of 6×10^{-5} M nitrite, to which varying amounts of possible interferences were added. The tolerance limit was taken as the amount which caused an error of less than 5% for the determination of 6×10^{-5} M nitrite. The results were summarized in Fig.7. Most of the interferences have no influence on the determination of nitrite, because the acidic medium

could highly reduce the interference from the transition metals. Therefore, the results indicated that the proposed CL system is highly selective for nitrite.

3.6 Analytical applications.

In order to evaluate the applicability and reliability of the proposed method, it was applied to the determination of nitrite in real samples, such as tap water, pond water, and river water. From Table.2, it can be seen that the recovery of nitrite in real samples ranged from 95.5 to 110.2% through standard addition experiments, which demonstrated the proposed CL system was satisfactory for nitrite analysis. Meanwhile, the analytical results of the proposed method were evaluated by the national food safety standard (GB 5009.33-2010) [40]. As shown in Table.3, the results that obtained with the two methods were in accordance with the sample determination.

4. Conclusion

In summary, gold nanoclusters were first demonstrated as a catalyst in the ultra-weak CL system of peroxynitrous acid, which was formed by the online reaction of acidified H_2O_2 and $NaNO_2$. The acidic medium also could highly reduce the interference from the transition metals. The enhanced CL could be attributed to the catalysis of Au nanoclusters, which effectively catalyzed the decomposition of H_2O_2 to produce double hydroxyl radicals. With the advantage of the CL of ONOOH in the presence of gold nanoclusters, we have developed a sensitive, simple, and straightforward flow-injection CL method for nitrite determination. The established method has been successfully applied to the determination of nitrite in pond

water, tap water, and river water with good recovery and high reproducibility.

Acknowledgements

This work was supported by science and tecnology commission foundation of Chongqing (CSTC, 2010BB8328)

We thank Prof. H. Z. Zheng and Prof. Y. M. Huang for measurements.

Figure captions

Scheme.1. Possible mechanism for the Au NCs-$NaNO_2$-H_2O_2 system.

Fig.1. Schematic diagram of the flow-injection manifolds for Au NCs-$NaNO_2$-H_2O_2 detection system. P1, P2 stand for two peristaltic pumps for solution delivery. R1: H_2O as the carrier; R2: Au NCs; R3: H_2O_2.

Fig.2. A: CL kinetic curves of $NaNO_2$-H_2O_2 system (curve 1) and Au NCs-$NaNO_2$-H_2O_2 system (curve 2). B: CL kinetic of H_2O_2 and the Au NCs-H_2O_2 system. Experimental condition: 0.2 M H_2O_2 in 0.04 M H_2SO_4, 8.0×10^{-6} M Au NCs, flow rate was set as 2.0 mL/min.

Fig.3. Effect of (A) the concentration of H_2SO_4, (B) the concentration of H_2O_2 (C) the concentration of Au NCs (D) the flow rate on the flow-injection CL detection system.

Fig. 4. CL spectrum of the Au NCs-$NaNO_2$-H_2O_2 system. (Experiment conditions: the PMT voltage was set at 700V, and the slit width of excitation and emission was 5 nm.)

Fig.5. UV-vis absorption of the reagent in the CL reaction. Experimental condition: 0.2 M H_2O_2 in 0.04 M H_2SO_4, 8.0×10^{-6} M Au NCs, 6.0×10^{-5} M nitrite, flow rate was set as 2.0 mL/min.

Fig.6. Standard curve for the nitrite concentration in the range from 5×10^{-6}-1×10^{-4} M.

Experimental condition: 0.2 M H_2O_2 in 0.04 M H_2SO_4, 8.0×10^{-6} M Au NCs, 6.0×10^{-5} M nitrite, flow rate was 2.0 mL/min.

Fig.7 Selectivity for nitrite assay against some interfering species with respect to 6.0×10^{-5} M nitrite. The concentration of some species (NO_3^-, Na^+, SO_4^{2-}, Cl^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, K^+, Mg^{2+}, F^- and glucose) was 10 mM; 1 mM for Ca^{2+}, Zn^{2+} and NH_4^+; 0.1 mM for Fe^{3+}, Cu^{2+}, malic acid and citric acid; 0.01 mM for I^-. Experimental condition: 0.2 M H_2O_2 in 0.04 M H_2SO_4, 8.0×10^{-6} M Au NCs, flow rate was set as 2.0 mL/min.

Tables:

Table.1 Effect of different radical scavengers on the CL of nitrite-H_2O_2 in the presence of Au nanoclusters[a]

Scavengers	Intermediates	Concentration	Percent inhibition[b](%)
H_2O			0
NaN_3	$^1O_2$	5mM	6
Ascorbic acid	$OH^{\cdot}$,$O_2^{\cdot-}$	1mM	26.5
NBT	$O_2^{\cdot-}$	1mM	60.0
Thiourea	$OH^{\cdot}$	5mM	61.1

[a]Solution condition: 0.2 M H_2O_2 in 0.04 M H_2SO_4, 8.0×10^{-6} M AuNCs, 6×10^{-5} M nitrite.
[b]Average value of three determination.

Table 2 Result of recovery test on nitrite determination (n =3) for water samples.

Samples	Added (10^{-5} M)	Found (10^{-5} M)	Recovery (%)
Tap water	2	1.91±0.01	95.5
	3	3.16±0.04	105.3
	8	8.01±0.01	100.1
Pond water	6	6.04±0.04	100.6
	8	7.67±0.03	95.9
	9	8.99±0.01	99.9
River water	2	2.03±0.03	101.5
	4	4.41±0.01	110.2
	6	5.90±0.02	98.3

Table 3 Determination of nitrite in water samples (n=3).

Samples	Proposed method Nitrite(10^{-5} M)	spectrophotometric method[a] (10^{-5} M)
Tap water	1.91±0.01	1.96±0.02
Pond water	6.04±0.04	6.10±0.02
River water	2.03±0.03	1.97±0.02

[a]Data taken from ref 34.

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Fig.1

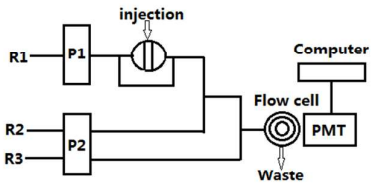


Fig.2(A)

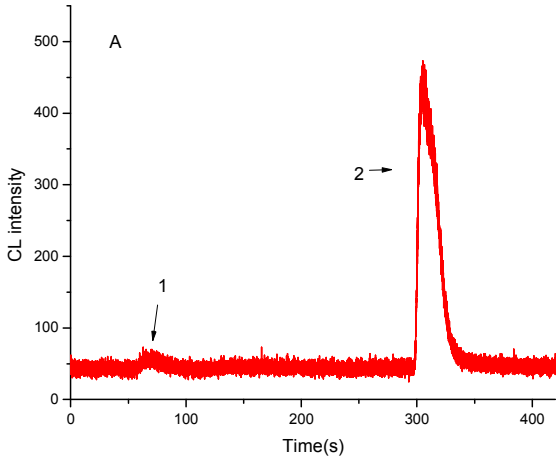


Fig.2(B)

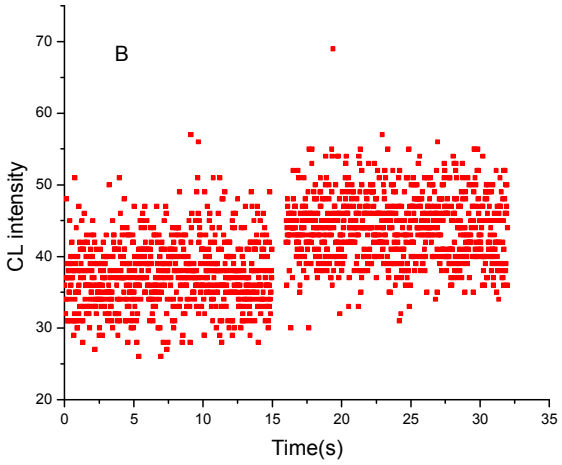


Fig.3(A)

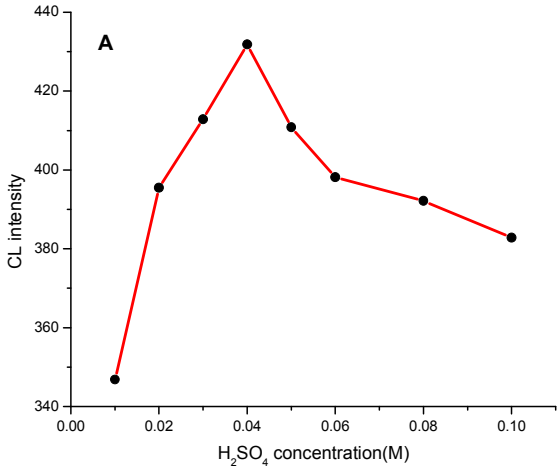


Fig.3(B)

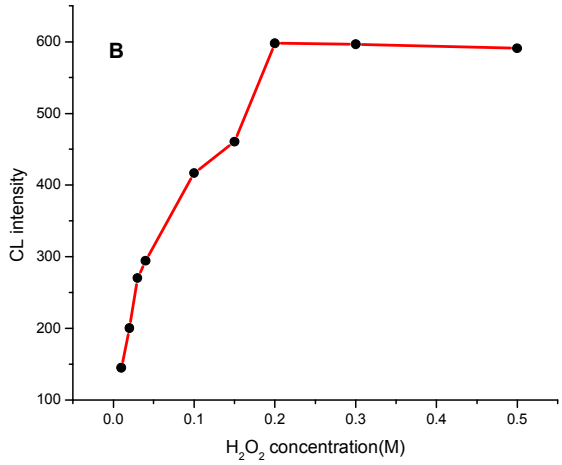


Fig.3(C)

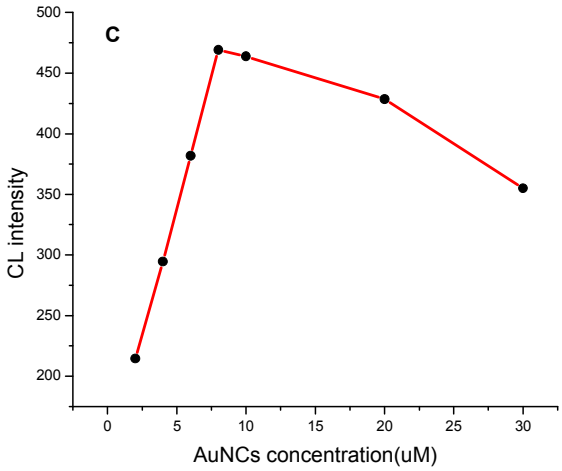


Fig.3(D)

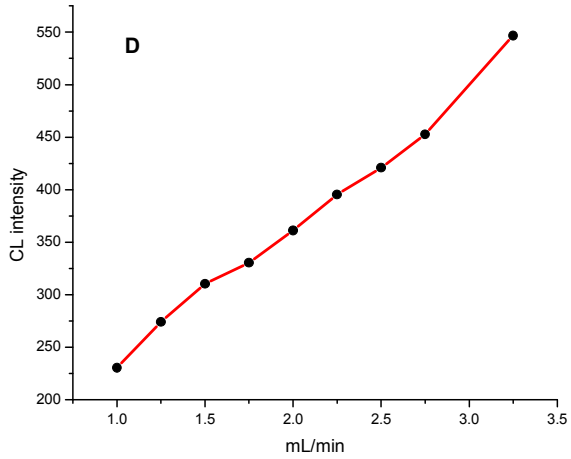


Fig.4

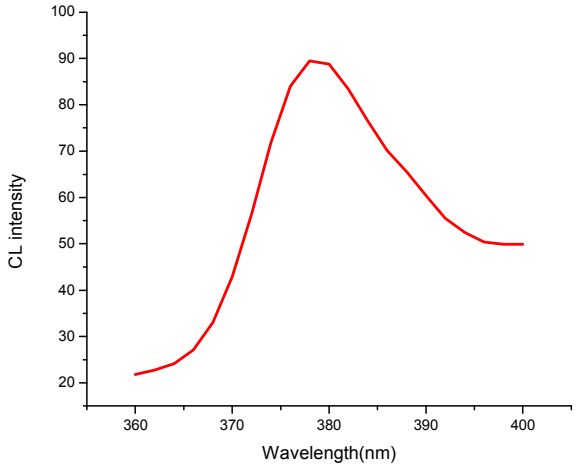
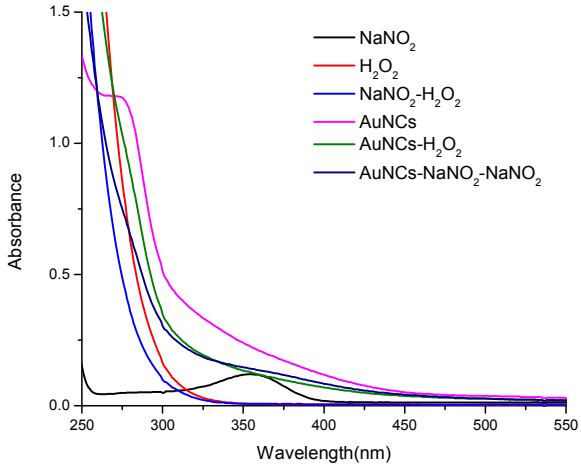


Fig.5



Scheme.1

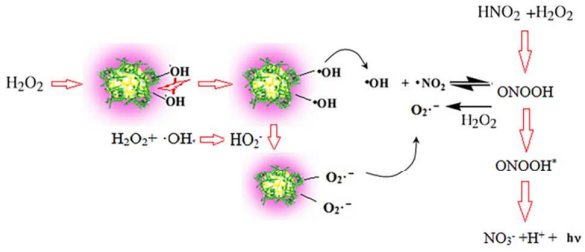


Fig.6

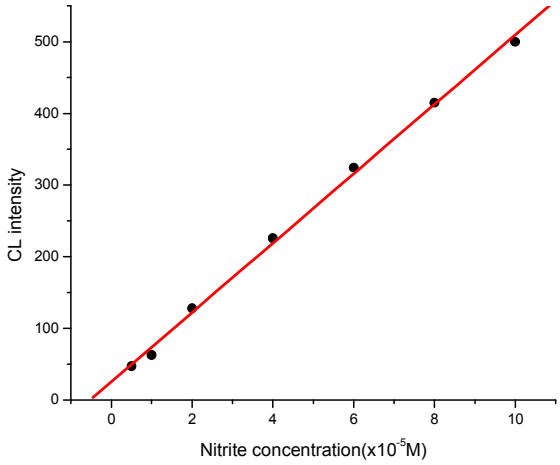
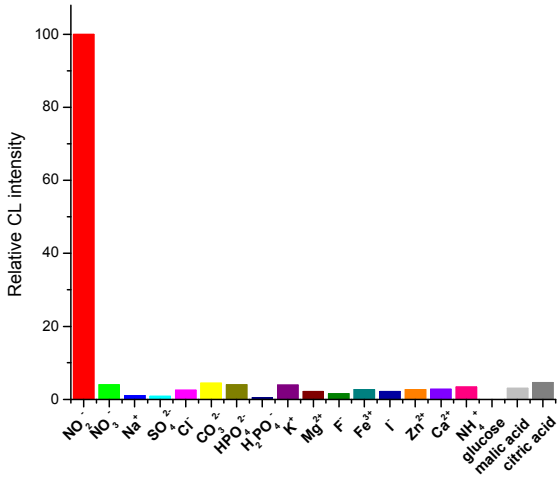
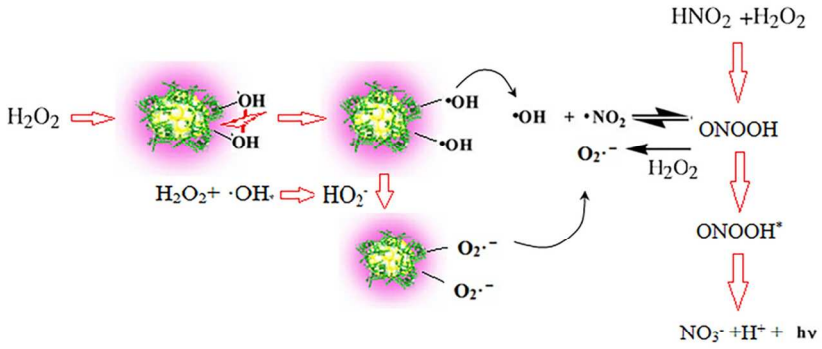


Fig.7





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