A Highly Efficient Chemiluminescence System Based on an Enhancing Effect of Ag Nanoclusters/Graphene Quantum Dots Mixture for Ultrasensitive Detection of Rabeprazole

Ashraf YOUSEFZADEH,* Jafar ABOLHASANI,** Javad HASSANZADEH,* and Mohammad Hossein SOMI***

*Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran
**Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran
***Liver and Gastrointestinal Diseases Research Center, Tabriz University of Medical Sciences, Tabriz, Iran

Herein, an efficient chemiluminescence (CL) reaction with a high emission intensity is reported based on a synergistic improving effect of silver nanoclusters (AgNCs) and graphene quantum dots (GQDs). First, the syntheses of AgNCs and GQDs were simply performed by the chemical reducing of AgNO₃ and a thermal treatment of glucose, respectively. After the characterization steps, the beneficial behavior of the prepared nanomaterial was investigated in CL systems. The oxidation reaction of KMnO₄-rhodamine B produced weak CL emission. However, the presence of AgNCs and GQDs led to a synergetic enhancing effect, and thus higher emission was obtained. A possible mechanism was investigated for this effect using absorption and fluorescence experiments. Furthermore, rabeprazole showed a relatively selective enhancing impact on the CL emission. The CL intensity was linearly increased in the rabeprazole concentration range of 4 – 133 ng mL⁻¹ with a detection limit (3σ/m) of 1.1 ng mL⁻¹. The developed CL method was utilized for the measurement of Rbp in biological samples with acceptable precision and accuracy.

Keywords Ag nanoclusters, graphene quantum dots, amplifying effect, chemiluminescence, rabeprazole

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Introduction

Rabeprazole sodium (Rbp, 2-[[4-(3-methoxypropoxy)-3-methyl-2-pyridinyl]-methyl] sulfonic-1H-benzimidazole sodium salt), as a potent proton pump suppressor, is usually applied to inhibit the gastrointestinal secretion of gastric acid. This action is useful in medical usages for the managing of hyper-secretory conditions (excess gastric acid creation). Rbp performs its role by reaching into the secretory canaliculus of the stomach parietal cells and suppressing enzymatic hydrogen potassium adenosine triphosphatase (H⁺/K⁺ ATPase) acid pumps. In acidic media, Rbp turns into a reactive sulfonamide intermediate, which can perpetually link the cysteine residues, producing disulfide product. Thus, the pump configuration alters, and acid secretion is suppressed.¹ The activation process of Rbp is more rapid than other proton pump inhibitors.² The most reported side effects for Rbp comprise headache, diarrhea and nausea. However, some serious signs have also been reported, including hepatotoxicity, rashes, and infections. In addition to these undesirable properties, the rapid and simple measurement of drugs, like Rbp in pharmaceutical or biological samples, is essential for the quality control or research laboratories. There are varied reports concerning the detection of Rbp, generally based on chromatography¹–⁶ and spectrophotometric techniques.⁷–⁹

These methods are mostly time-consuming, expensive, and require some additional pretreatment processes. The spectrophotometric methods also have low sensitivity and poor reliability.

In contrast, chemiluminescence (CL), light emission during the chemical reactions, is a powerful procedure to layout favorable assays for the detection of different analytes.¹⁰ The great attraction toward CL-based analytical approaches is due to its matchless benefits, involving simple and rapid detection, high sensitivity and an excellent detection limit, economical instrumentation, and broad linear dynamic ranges. Besides, the applicability of CL systems was recently extended using different helpful nanomaterials,¹⁰–¹⁴ such as metal/metal oxide¹⁵ and carbon nanostructures.¹⁴ They can acts as emitters, catalysts or energy acceptors in CL systems, and thus can lead to a valuable improving effects on the obtained emission.¹⁰

Noble-metal nanoclusters, with their ultra-small size (<1 nm, nearby the Fermi-wavelength of conduction electrons), have superior features,¹⁶–¹⁷ involving water solubility, good biocompatibility, high photo-stability and strong quantum-confinement impact with size-tunable electronic transitions.¹⁶–¹⁸ The strong optical properties, high fluorescent nature and great stability of silver nanoclusters (AgNCs) have make them suitable choices to design sensing probes or bio-imaging aims.¹⁹,²⁰ They have been widely employed in CL systems.²¹–²³ On the other hand, graphene quantum dots (GQDs) are shaped from small graphene segments, which have recently been turned into more interesting nanomaterials.²⁴,²⁵ This attention is due to their excellent advantages, like high solubility and photo-
Apparatus
The CL signals were evaluated by a Sirius L single tube luminometer (Berthold, Germany). Fluorescence and UV-Vis absorption analysis was carried out using an RF-5301 spectrophotofluorometer (Shimadzu, Japan) and UV-1800 spectrophotometer (Shimadzu, Japan), respectively. The CL spectra were obtained by a flow-based system connected to the same spectrophotofluorometer while the excitation source had been turned off. Some techniques were used to investigate the morphology and chemical conditions of synthesized AgNCs and GQDs, using a JEOL high-resolution transmission electron microscope (HR-TEM, JEM-2200FS, Japan), a Fourier transform infrared (FT-IR) spectrometer (Sensor 27, Bruker, Germany) and an X-ray diffractometer (D5000, Siemens, USA) with a Cu Kα radiation source (1.54065 Å).

Synthesis processes
AgNCs was synthesized by a simple route,29 including the addition of NaBH₄ into a mixed Ag⁺ and stabilizer solution. Typically, a NaOH solution (110 μL, 1 M) was added into a 4 mL Ag⁺ aqueous solution (containing 10 mM AgNO₃ and 0.05 g mL⁻¹ BSA, stirred for at least 3 min). The solution was vigorously stirred, followed by a drop-wise addition of 150 μL of a NaBH₄ solution (10 mM). Stirring was continued until the color of the solution gently varied from colorless to reddish brown. This change indicated the formation of AgNCs. The prepared solution of AgNCs was maintained at 4°C before its usage. Different sizes of AgNCs were synthesized using the same process, in the presence of different concentrations of silver ions. Also, silver nanoparticles of deferent sizes and shapes were synthesized for comparison experiments, as in reported literature.30-32

GQDs were simply synthesized by the thermal pyrolysis of pure glucose powder.31 Briefly, 6.0 g of glucose was liquefied at 180°C (using a magnetic hotplate stirrer, IKA RH basic 2, Germany). Upon continuing the thermal treatment, a color change occurred to dark orange, which showed the formation of GQDs. Heating was continued for another 2 min, and then some DI (25 mL) was gradually poured into the solution. Eventually, the GQDs solution was sealed and kept at 4°C.

General procedure for chemiluminescence detection of rabeprazole
CL experiments for the measurement of Rbp were performed in a batch system: 240 μL H₂SO₄ (1 M) solution, 300 μL RhoB (1 mM) solution, 600 μL of synthesized GQDs solution, 90 μL of the gained AgNCs solution as well as a certain volume of the Rbp standard or its sample solution (100 μL) were respectively transferred into a luminometer cuvette (with a total volume of 4 mL). The final volume of the solution reached 3 mL by DI. Then, the solution was placed into a sample container of the luminometer, and a 60-μL KMnO₄ (7 mM) solution was automatically added to commence the CL reaction. The produced CL emission was followed during the time, and the generated maximum CL intensity was selected as an analytical signal.

Experimental
Reagents and chemicals
The materials applied in the present work were all of analytical grade, and deionized water (DI) was used in the preparation of all solutions. Silver nitrate (AgNO₃), glucose, bovine serum albumin (BSA), sodium borohydride (NaBH₄), potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄), rhodamine B (RhoB) and the other used chemicals were purchased from Merck (Germany, www.merck-chemicals.com). A rabeprazole stock solution (1000 μg mL⁻¹) was prepared by dissolving an appropriate amount of rabeprazole sodium powder (Abourihan Pharmaceutical Factory, Tehran, Iran) in DI. Also, to prepare stock KMnO₄ (7 mM) and RhoB (1 mM) solutions, 0.111 g of KMnO₄ and 0.048 g of RhoB powder were exactly dissolved in DI, respectively, and were then diluted to 100 mL.

Stability, chemical inertness, tunable luminescence, facile functionalization, great electrical and thermal conductivity.26-28 There are some reports concerning the contribution of GQDs in CL-based assays, which have demonstrated important benefits. AgNCs and GQDs have attached a great regard in luminescence-based procedures. But, to the best of our knowledge, there is no report about the synergetic improving effect of AgNCs and GQDs. Herein, the simultaneous and considerable improving effects of AgNCs and GQDs on the weak emission intensity of KMnO₄-rhodamine B (RhoB) CL system have been reported. The insertion of mixed AgNCs/GQDs could impressively enhance the CL emission intensity obtained from the oxidation of RhoB. This effect was related to energy transferring that occurred between the CL reagents or GQDs could impressively enhance the CL emission intensity of KMnO₄-rhodamine B (RhoB) CL system. So, a sensitive CL method was designed for the quantitative analysis of Rbp in human biological samples (Fig. 1). This method provides many benefits for the analysis of Rbp, such as simplicity, accuracy, rapidity, reliability and a vast linear range.

Fig. 1 Design for the detection of rabeprazole by the developed CL system.
Results and Discussion

Characterization of synthesized nanomaterials

The correct preparation of AgNCs was easily verified by HR-TEM images (Fig. 2A). According to the HR-TEM images, the diameter size of AgNCs was assessed to be in the range of 0.5 - 1.5 nm, with an average value of 0.9 nm (measured by more than 100 particle). Besides, the TEM image of prepared GQDs verified the monotonous dispersity of synthesized GQDs (Fig. 2B). The sizes of GQDs were in a narrow range with an intermediate diameter of 17.6 ± 2.9 nm. As can be seen from inset in Fig. 2B, a crystal lattice with a layer distance of 0.24 nm was apperceived for a single QD using the HR-TEM illustration. It was equal to the (1120) lattice parameter of the graphene layered structure.

X-ray diffraction (XRD) patterns (Fig. 2C) were employed to study the crystalline features of synthesized nanomaterials. The achieved XRD pattern for AgNCs showed a number of clear peaks, mainly located at 2θ values of about 38.1 and 44.3°, which were responsible for the (111) and (200) planes. Also, a graphite-like structure for synthesized GQDs was obtained by its special broad diffraction peak (002) at about 18° in XRD spectrum (Fig. 2C). On the other hand, the FT-IR spectra for AgNCs and GQDs are shown in Fig. 2D. As can be seen, the main absorption bonds for AgNCs contain 1232, 1351 and 1557 cm⁻¹ which are related to the amide groups of BSA on the surface of NCs (C –N stretch coupled with N –H bending mode and C =O stretch, respectively). Also, the C –H bonds and N–H/O–H stretching vibrations peaks were observed at about 2988 and 3318 cm⁻¹, respectively. The FT-IR spectrum of GQDs (Fig. 2D) illustrated the absorption peaks for the
stretches vibrations of C=O, C=C and C-H bonds to be at about 1645, 1365 and 2928 cm⁻¹, respectively. Also, the lean peaks at 3342 and 1035 cm⁻¹ were related to the O-H stretching vibrations and C-O bonds, respectively.

Finally, the optical properties of the prepared nanostructures were investigated. The BSA-stabilized AgNCs displayed broad absorption at low wavelengths, without any particular surface plasmon resonance peak above 300 nm (Fig. 2E). Also, the gained NCs could cause a high fluorescence emission, with a relatively broad peak from 550 to 780 nm. The maximum emission intensity was located at a wavelength of about 650 nm ($\lambda_{\text{em}} = 280$ nm) (Fig. 2E). A quantum yield (QY) of 9.1% was computed using rhodamine B as a reference material.

UV-vis absorption spectrum for GQDs illustrated two main peaks at nearly 229 and 277 nm (Fig. 2F), which were linked to the $\pi \rightarrow \pi^*$ (in aromatic rings) and $n \rightarrow \pi^*$ (in carbonyl groups) transitions, respectively. In addition, in accordance to the fluorometric analysis, a powerful fluorescence emission was shown for the prepared GQDs (Fig. 2F); its maximum emission wavelength ($\lambda_{\text{em}}$) was dependent on the excitation wavelength ($\lambda_{\text{ex}}$). The optimum emission was obtained by $\lambda_{\text{em}} = 360$ nm, which showed a quantum yield of 46% at 440 nm (rhodamine B was used as reference fluorescent material). It is better to state that the synthesized AgNCs and GQDs were stable for at least 4 months, when they were reserved at 4°C.

**Chemiluminescence reaction sensitized by Ag NCs and GQDs**

As one of the most common oxidants applied in CL systems, KMnO₄ can rapidly react with some organic dyes and produce CL emission. Herein, the KMnO₄-RhoB reaction was applied to test the promoting effect of the synthesized nanomaterial. A relatively weak CL is generated in this system, which has been described in some reports. The CL emission profiles during the time are shown in Fig. 3A. A clear enhancement in the CL intensity was observed upon adding AgNCs or GQDs (Fig. 3A, curves b - f). However, the simultaneous presence of AgNCs and GQDs led to a great promoting effect (Fig. 3A, curve g). The experiments showed that in the presence of AgNCs and GQDs, the CL reaction occur rapidly, and the emission peak was created in a relatively shorter time than the only RhoB system (Fig. 3A). Also, AgNCs could accelerate the CL emission of GQDs contained systems (compare graphs d with f and e with g in Fig. 3A), showing the catalytic activity of AgNCs in these systems. Comparison experiments were performed to investigate the effect of nanoclusters sizes (Table S1, Supporting Information). Also, silver nanoparticles (AgNPs) with different sizes and shapes were applied in the developed system. The results are indicated in Table S1. As is clear, AgNCs with an average sizes of 0.9 nm provided the best enhancing effect. They were thus selected as the optimal nanostructures for CL experiments.

Furthermore, the CL spectra were plotted for the considered CL system to investigate the nature of the emitting species (Fig. 3B). Interactions between KMnO₄ and RhoB in an acidic condition induce a characteristic CL emission peak at around 580 nm (Fig. 3B, spectrum a), which is similar to RhoB fluorescence spectrum (excitation wavelength = 558 nm). This means that the RhoB molecules act as the main emitting species in the CL reaction. They can be excited through energy transfer from excited intermediate species. The observed emission can be elucidated according to the former studies. Oxidation of RhoB by KMnO₄ produces some excited intermediate species (RhoB$^*$) (reaction 1), which can emit at about 425 nm. This intermediate product has been accepted as the emitting species in some reports for the Ce(VI)-RhoB CL system. An energy transferring process between the RhoB$^*$ and free RhoB can also produce excited RhoB$^*$. However, the little overlap between the emission of RhoB$^*$ and the excitation spectrum of RhoB led to an inefficient energy transfer, and thus the observed CL peak at 580 nm is weak. Besides, direct oxidation of GQDs or AgNCs could generated CL emission at about 480 and 650 nm, respectively (Fig. 3B, spectra b and c). These emission peaks can be related to the high-energy intermediate species, which transfer energy to GQDs or AgNCs, to produce GQDs$^*$ and AgNCs$^*$, respectively. The decrease in the fluorescence emission intensity of RhoB, AgNCs and GQDs also verified that KMnO₄ can directly oxidize each of them.

The peak at 580 nm was the main emission for the KMnO₄-RhoB-AgNCs system, too. The low speed of the KMnO₄-AgNCs reaction in the applied condition is the reason why no emission was observed at 650 nm (Fig. 3B, spectrum d). On the other hand, two emission peak at 480 and 580 nm were created for the KMnO₄-RhoB-GQDs system (Fig. 3B, spectrum e). The first emission peak can be related to the excited GQDs$^*$ species, which is produced by the direct oxidation of GQDs, similar to the KMnO₄-GQDs system. A second possible way to generate GQDs$^*$ can be considered to be exciting GQDs by the energy of the RhoB$^*$ species. There is a considerable overlap between the emission of RhoB$^*$ and the excitation spectrum of GQDs, at 425 nm. Thus, an effective energy transfer can occur between them (reaction 2). The observed peak at 580 nm can also be linked to the RhoB$^*$ species, produced by subsequent energy transferring from GQDs$^*$ to RhoB molecules (reaction 4). The emission of GQDs$^*$ at 480 nm is relatively near to the excitation spectrum of RhoB, and the energy transfer can effectively occur between them. Thus, the CL peak at 580 nm has a higher intensity than that of the KMnO₄-RhoB system.

**Fig. 3** A) CL time profiles and B) CL spectra for different solutions after the addition of KMnO₄.
An investigation of the KMnO₄-GQDs-AgNCs system (Fig. 3B, spectrum f) showed just one emission peak at 480 nm, with a light increase in the intensity. Finally, when the AgNCs was added to the KMnO₄-GQDs-RhoB system (Fig. 3B, spectrum g), a remarkably increasing effect was caused for the peak at 580 nm. A slight increase was also observed for the CL peak at 480 nm. These observations verified the improving effect of AgNCs on the stability of the RhoB*-• intermediates. AgNCs can adsorb RhoB or its intermediate species and increase the stability of the emitting species RhoB*-•. By the way, the great enhancing effect on the peak at 580 nm strongly demonstrates the contribution of AgNCs in the energy transferring processes (reactions 2, 4). AgNCs keep the reactants together, and increase the probability of energy transfer between them. The decrease in the fluorescence emission of AgNCs in the presence of RhoB or GQDs, confirmed their interactions.

In summary, the synergetic improving effect of mixed AgNCs/GQDs on the CL emission of KMnO₄-RhoB is connected to the simultaneous cooperation of GQDs in the energy transferring process and the facilitating effect of AgNCs on the energy transferring processes (reaction 2):

RhoB + KMnO₄ → [RhoB*-•] + Mn²⁺  (1)

[RhoB*-•] + GQDs (AgNCs as catalyst) → [RhoB*] + GQDs* (2)

GQDs* → GQDs + hυ (480 nm) (3)

GQDs* + RhoB (AgNCs as catalyst) → GQDs + RhoB* (4)

RhoB* → RhoB + hυ (580 nm) (5)

Rabeprazole effect
The experiments showed that the CL signal of the KMnO₄-RhoB-AgNCs/GQDs system was considerably enhanced by the existence of Rbp. The Rbp absorption at about 295 nm was affected by the addition of KMnO₄. It can thus be considered that Rbp can be oxidized by KMnO₄, resulting in the generation of high-energy intermediates. The energy of these intermediates are transferred to GQDs or RhoB, and increase the concentration of the emitting species. Anyhow, the observed increased effect was proportional to the Rbp concentration, and can be used as a design for a quick and susceptible route for the measurement of Rbp.

Optimization
The reaction condition, such as the concentrations of KMnO₄, RhoB, GQDs and AgNCs, were optimized for the CL system in order to obtain the highest analytical signal for rabeprazole (Fig. S1, Supporting Information). ΔI = I₀ – I was considered to be the CL signal, which covers the difference between the CL intensity of the KMnO₄-RhoB-AgNCs-GQDs system with (I₀) or without Rbp (I). As can be seen from Fig. S1A, ΔI was slightly enhanced upon increasing the RhoB concentration up to 0.1 mM, and was then reduced. The reduction at high levels of RhoB can be due to the self-absorption impact. Figure S1B shows the effect of the HSO₄⁻ concentration. The highest CL emission was gained with a HSO₄⁻ concentration of 0.08 M, which is the result of the compliance between the reaction kinetic enhancement and more aggregation of the nanomaterial in upper HSO₄⁻ concentrations.

On the other hand, GQDs have a great enhancing impact (Fig. S1C) on ΔI, because of its high efficacy in the energy transferring process. The effect of the AgNCs concentration was also studied (Fig. S1D). AgNCs enhanced the CL response from 20 to 90 μL, and then decreased in amounts greater than 90 μL. The decrease occurred in higher concentrations of GQDs or AgNCs, was probably related to the interaction of excess GQDs and/or AgNCs with KMnO₄. Finally, the effect of the KMnO₄ concentration on CL was also tested in the range of 7 × 10⁻⁴ to 2.8 × 10⁻⁴ M. As Fig. S1E shows, the optimal KMnO₄ concentration was set at 1.4 × 10⁻⁴ M.

Analytical features
Based on the increasing effect of Rbp on the CL intensity of the KMnO₄-RhoB-AgNCs-GQDs system, an ultrasensitive assay was developed. This effect is shown in Fig. 4A for different concentrations of Rbp. The linear calibration graph (Fig. 4B) was obtained in the range of 4-133 ng mL⁻¹ (ΔI = 11.9C + 9.2, R² = 0.9972). The limit of detection (LOD) was also 1.1 ng mL⁻¹ (calculated 3σ/m). C, m and σ show the standard deviation of signal for blank solution and the slope of calibration graph, respectively). Besides, the relative standard deviations (RSD%) were 1.32 and 2.51%, acquired for five replicate measurements of 30 and 100 ng mL⁻¹ of Rbp, respectively.

Comparisons between the presented CL method and some other reported methods for the measurement of Rbp are shown in Table 1. As can be seen, the offered CL technique is comparable with others, and has good sensitivity. It has a high potential for reliable, rapid and cost-effective measurements of Rbp.

Interference study
To check the selectivity of the presented method, it was used for the determination of Rbp with a constant concentration...
of Rbp. Rbp has an enhancing effect on the CL intensity, applied for the reliable, sensitive, simple and rapid quantification intensity. As a useful application, the developed CL system was GQDs and RhoB is the reason for the enhancement of the CL oxidation products and GQDs, and also between the excited spectra and kinetic profiles. It was shown that the facilitating the emitted CL emission intensity by several orders. The AgNCs and GQDs in the CL system of KMnO$_4$-RhoB enhanced was developed. It was shown that the simultaneous presence of amounts added and recovered.

**Analytical application study**

The developed method was used for the quantification of rabeprazole in human urine samples. The real samples, after the spiking of certain amounts of the Rbp standard solution, were provided according to the details of the real samples preparation procedure (described in Supporting Information). They were then analyzed by the presented method (Table S3, Supporting Information); statistical analysis of the outcomes with the t-test showed that there is no remarkable differences between the amounts added and recovered.

**Conclusions**

In summary, a new CL system based on RhoB oxidation by KMnO$_4$, and a synergetic improving effect of AgNCs and GQDs was developed. It was shown that the simultaneous presence of AgNCs and GQDs in the CL system of KMnO$_4$-RhoB enhanced the emitted CL emission intensity by several orders. The mechanism of this CL reaction was studied based on the CL spectra and kinetic profiles. It was shown that the facilitating effect of AgNCs on the energy transfer between the RhoB oxidation products and GQDs, and also between the excited GQDs and RhoB is the reason for the enhancement of the CL intensity. As a useful application, the developed CL system was applied for the reliable, sensitive, simple and rapid quantification of Rbp. Rbp has an enhancing effect on the CL intensity, proportional to its concentration. The limit of detection was 1.1 ng mL$^{-1}$. Moreover, the method was acceptably employed for the measurement of Rbp in urine samples.

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**Supporting Information**

The details for sample preparation, Table S1 (Interfering studies), Table S2 (results for real samples) and Fig. S1 (optimization graphs) are placed in Supporting Information file. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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