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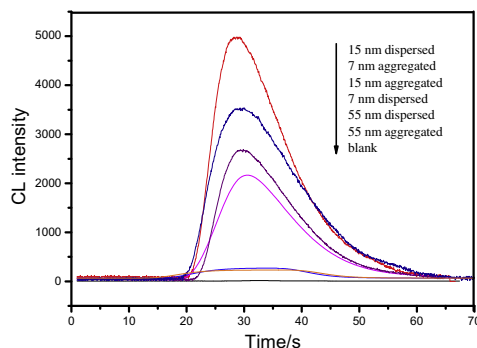
## Effect of aggregated silver nanoparticles on luminol chemiluminescence system and its analytical application

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### HIGHLIGHTS

- For AgNPs's catalysis on luminol CL system, aggregation was an important factor.
- The aggregated AgNPs's effect characteristic was closely related to AgNPs's sizes.
- Aggregation led to CL increase for 7 nm, decline for 15 nm and no change for 55 nm.
- Aggregated AgNPs's effect is due to electron density's change in conduction band.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We found that after silver nanoparticles (AgNPs) aggregated, its catalytic activity on luminol CL reaction obviously changed, and the change characteristic was closely related to the sizes of AgNPs. UV–visible spectra, X-ray photoelectron spectra, zeta potential and transmission electron microscopy studies were carried out to investigate the CL effect mechanism. The different CL responses of aggregated AgNPs with different size were suggested to be due to the two effects of quantum size and electron density in nanoparticle's conduction bands, and which one played a major role. The poisonous organic contaminants such as anilines, could induce the aggregation of AgNPs, were observed to affect effectively the luminol–H<sub>2</sub>O<sub>2</sub>–7 nm and 15 nm AgNPs CL systems and were detectable by use of a flow injection method with the enhanced or inhibited CL detection.

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### Introduction

Metal nanomaterials have received significant attention for their special characteristics such as quantum size effect, surface effect, macro-quantum tunnel effect [1,2] and their potential applications in microelectronics, optics, electronics, magnetic devices, and catalysis [3–5]. Silver nanoparticles (AgNPs), mostly hydrosols, are perhaps most widely studied because of their important

applications in catalysis [6–8], photographic processes, intrinsic antimicrobial properties, and surface-enhanced Raman spectroscopy (SERS) [9,10]. Ag<sup>+</sup> is one rather strong oxidant. With the lower redox potential ( $E^{\circ}_{Ag^+/Ag} = +0.799$  V), silver has the better chemical activity than gold and platinum.

Chemiluminescence (CL) is known as a powerful and important analytical technique, because of its extremely high sensitivity along with its other advantages, such as simple instrumentation, wide calibration ranges, and suitability for miniaturization in analytical chemistry [11,12]. The catalysis of nanoparticles for CL reactions becomes an expanding area in recent years

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[6–8,13–19]. As silver has the better chemical activity than gold and platinum, many studies on AgNPs catalytic CL system have been reported [8,20–25]. In 2007, AgNPs were firstly applied into CL system and it was found that AgNPs could catalyze the luminol–H<sub>2</sub>O<sub>2</sub> CL reaction [8]. Afterward, AgNPs were used as catalysts in other CL reactions [20–25]. In 2010, Haghghi' group [20] investigated the effect of AgNPs on the luminol–isoniazid system. Cui et al. [21] found that AgNPs in the presence of nucleophiles and Cu<sup>2+</sup> could induce luminol to produce CL. A flow injection CL determination of norfloxacin (NFLX) was developed based on the Ce(IV)–Na<sub>2</sub>SO<sub>3</sub> redox system in the presence of AgNPs [22]. In 2011, Liu and Li [23] developed AgNPs–luminol–AgNO<sub>3</sub> CL system and used the CL system in immunoassay for IgG. Chen et al. [24] reported that bisphenol A (BPA) could inhibit AgNPs–enhanced luminol–KMnO<sub>4</sub> CL system and realized CL detection of BPA. Very recently, Liu et al. [25] developed a CL method for the determination of nitrofurans (NFs) based on the luminol–H<sub>2</sub>O<sub>2</sub>–AgNPs CL system. Indeed, AgNPs exhibited a better CL catalysis ability than gold and platinum nanoparticles [15,23].

In general, the catalysis of nanoparticles for CL system was found to be related to their size [8,13], surface state [26], and morphology [27–29]. Certainly, different state of aggregation of nanoparticles may also influence their catalytic activity for CL system. Actually, the aggregation of AgNPs is a frequent phenomenon and can occur in the presence of salt or organics [30–33]. It was reported that aniline and their derivatives could induce the aggregation of AgNPs [30]. Hence, the catalytic activity of AgNPs on CL system may be changed when they are transformed from dispersion to aggregation. The applicability of aggregated AgNPs used in the direct CL assay determination of the poisonous organic contaminants such as aniline and their derivatives depends on whether or not the aggregated AgNPs induced by the poisonous organic contaminants show different catalytic activity for the CL reaction.

In this work, we chose luminol–H<sub>2</sub>O<sub>2</sub> CL reaction as model system and the systematic study regarding the difference of the catalysis behavior for CL reaction between dispersed and aggregated AgNPs was conducted. The catalytic mechanism of aggregated AgNPs on luminol–H<sub>2</sub>O<sub>2</sub> CL reaction was investigated. The aniline and their derivatives, which could induce the aggregation of AgNPs, were detectable by luminol–H<sub>2</sub>O<sub>2</sub>–7 nm and 15 nm AgNPs CL system combined with a flow injection method with the enhanced and inhibited CL detection, respectively.

## Experimental

### Chemicals and solutions

Luminol stock solution ( $2.5 \times 10^{-2}$  M) was prepared by dissolving 4.43 g luminol (obtained from Shaanxi Normal University, Xi'an, China) in 20 mL of 0.10 M NaOH and then diluting to 1 L with water. The luminol solution was stored in dark for one week prior to use ensured that the reagent property was stabilized. Working solutions of luminol were prepared by diluting the stock solution. Working solutions of H<sub>2</sub>O<sub>2</sub> were prepared fresh daily from 30% (w/w) H<sub>2</sub>O<sub>2</sub> reagent solution (Shanghai Chemical Plant, Shanghai, China). AgNO<sub>3</sub>, trimethyl ammonium bromide (CTAB), hydrazine hydrate, ethylenediamine and NaBH<sub>4</sub> were obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Sodium citrate, aniline, o-phenylenediamine, p-phenylenediamine and m-phenylenediamine were purchased from Tianjin Chemical Reagent Company (Tianjin, China). Other reagents and chemicals were of analytical grade and used without further purification. Doubly distilled and deionized water was used throughout.

### Apparatus

The CL intensity was measured and recorded with a model IFFL-D chemiluminescence Analyzer (Xi'an Ruimai Electronic Sci. Tech. Co., Ltd., Xi'an, China). Absorption spectra were recorded on a TU-1901 UV–visible spectroscopy (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). The transmission electron microscopy (TEM) images of AgNPs were taken using a JEM-2100 TEM (Japan Electronics Co., Ltd.). The CL spectra of this system were recorded with a Hitachi FL-4600 spectrofluorometer (Tokyo, Japan) combined with a flow-injection system, with its excitation source turned off. The X-ray photoelectron spectra (XPS) analysis of AgNPs before and after the CL reaction was performed with an ESCALab 220I-XL spectrometer. The determination of zeta potential was carried out by Malvern Zetasizer 2000.

### Preparation and characterization of AgNPs

All glassware used in these preparations was thoroughly cleaned in aqua regia (1:3 HNO<sub>3</sub>–HCl), rinsed in doubly distilled water, and oven-dried prior to use.

7 nm AgNPs were prepared according to the literature [34]. Firstly, after the pH value of 0.10 mol/L AgNO<sub>3</sub> aqueous solutions was adjusted to 10 with ethylenediamine, 10 mL of  $1 \times 10^{-3}$  mol/L cetyltrimethyl ammonium bromide (CTAB) was added to be mixed completely. Then 5 mL of the hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) solution was added to the above mixture drop-wise under vigorous stirring. Thereafter, the above mixture solution was kept to react under room temperature for 5 min, resulting in the formation of AgNPs, which was stored in 4 °C refrigerator before use.

15 nm AgNPs were prepared by the chemical reduction of silver nitrate in NaBH<sub>4</sub> according to the reported method [35]. Briefly, 25 mL  $1 \times 10^{-3}$  mol/L silver nitrate was added into 75 mL  $2 \times 10^{-3}$  mol/L fresh NaBH<sub>4</sub> solution drop-wise under vigorous stirring. After reacted for 10 min, 5 mL 1% (w/w) sodium citrate as stabilizer was added and continued to stir for an additional 30 min, and was left overnight before use.

55 nm AgNPs were prepared by the chemical reduction method according to the literature [36]. First, 100 mL of a solution containing AgNO<sub>3</sub> (0.4 mol/L), NaBH<sub>4</sub> (0.2 mol/L) and citric acid (0.4 mol/L) was prepared under vigorous stirring. The mixed solution was stirred for an additional 30 min to obtain dark brown AgNPs colloid and was left overnight before use.

The size and shape of the synthesized AgNPs were characterized by TEM. Statistical analysis of TEM data revealed that their average diameter (nm) was about  $7 \pm 2.5$ ,  $15 \pm 2.1$  and  $55 \pm 4.1$ , respectively, and their diameters were uniform and their dispersion was very good. In addition, UV–visible absorption spectra of the prepared AgNPs of various particle sizes were measured as shown in Fig. 1. The AgNPs of different particle sizes have different absorption spectra, which was consistent with the reports [34–36].

### Procedures for CL detection

A schematic diagram of the flow-injection CL system is shown in Fig. S1 luminol and H<sub>2</sub>O<sub>2</sub> were first mixed. Double distilled water was used as a carrier to carry the AgNPs solution to mix with luminol and H<sub>2</sub>O<sub>2</sub>. The solutions of luminol, H<sub>2</sub>O<sub>2</sub>, and double distilled water were pumped into the flow cell by the peristaltic pump at the rate of 1.6 mL/min, respectively. The AgNPs or the mixture solution of AgNPs and salt was injected by a valve injector with a 120  $\mu$ L sample loop. When the CL system was used for investigating the effects of target analytes on the CL system, the target analytes and AgNPs were first mixed and then injected by a valve injector. The CL signals were monitored by the PMT adjacent to the flow CL cell, and imported to the computer for data acquisition.

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