

# 纳米金参与的液相化学发光

## 摘 要

化学发光具有多年的研究历史。一直以来,有关液相化学发光的研究往往局限于分子和离子水平,以及简单的分子聚集体。最近,纳米粒子的液相化学发光行为已经引起了人们的关注。但是,目前对纳米粒子参与的液相化学发光的研究刚刚起步,仅有少量关于半导体纳米粒子液相化学发光的文献,对金属纳米粒子参与液相化学发光的研究尚未见报道。

本论文首先综述了化学发光研究的最新进展,以及纳米金的物理化学特性及其在分析化学中的应用现状,在此基础上选择纳米金为模型金属纳米粒子,研究了纳米金参与液相化学发光反应时的行为、规律、机理以及分析应用潜力等。主要研究内容如下:

1. 过氧化草酸酯(TCPO)与过氧化氢( $H_2O_2$ )的反应可以产生微弱的化学发光,我们发现粒径为2.6~6.0 nm的纳米金可以接受此反应释放的能量产生间接化学发光,其最大发射波长位于~415 nm。化学发光的强度与纳米金粒子的浓度之间存在良好的线性递增关系。对反应体系的荧光光谱、紫外可见吸收光谱、透射电镜(TEM)和X-射线光电子能谱(XPS)进行分析,在此基础上提出这一化学发光过程可能包含以下几个步骤:TCPO被 $H_2O_2$ 氧化生成高能量的中间体过氧环乙烷双酮(1,2-dioxetanedione);该中间体将能量传递给体系中共存的纳米金粒子而使纳米金被激发;激发态纳米金粒子在弛豫回到基态的过程中产生化学发光。总之,纳米金在此过程中被化学激发而产生光发射,其发光特性取决于纳米金的粒径,并且可能通过优化纳米金的粒径和表面状态而获得量子产率更高的化学发光体系。纳米金的这种化学发光特性与其优良的生物兼容性结合可能应用于发展新的生物分析方法。

2. 纳米金与 $KIO_4-NaOH-Na_2CO_3$ 之间的反应能够产生化学发光现象,该化学发光的光谱具有三个明显的发射带,分别位于380~390 nm、430~450 nm和490~500 nm。该体系的化学发光强度随着溶液中纳米金粒子浓度的增大而线性增加;并且当纳米金粒子表面柠檬酸根离子被 $SCN^-$ 离子取代时,体系化学发

光的强度显著增加。实验采用紫外可见吸收光谱、透射电镜 (TEM) 和 X-射线光电子能谱 (XPS) 技术研究了 CL 反应前后纳米金的形貌、粒径和氧化态, 在此基础上提出体系化学发光的机理可能是纳米金作为化学发光反应的微尺度反应平台, 与反应过程中生成的  $\text{CO}_3^{\cdot-}$  和  $\text{O}_2^{\cdot-}$  自由基相互作用, 在纳米金表面生成了 Au(I)络合物、二氧化碳双分子对以及单线态氧分子对的激发态而产生化学发光。

3. 在酸性介质中  $\text{KMnO}_4$  可以与纳米金发生氧化还原反应, 反应过程中伴随的化学发光现象取决于纳米金的粒径。对于粒径为 2.6 和 6.0 nm 的纳米金, 它们与酸性  $\text{KMnO}_4$  的反应速度快, 因此可以在 640 nm 左右产生化学发光, 并且化学发光的强度与纳米金粒子浓度之间存在良好的线性递增关系。对于粒径大于 6.0 nm 的纳米金, 由于与  $\text{KMnO}_4$  的反应速度较慢, 反应过程中并不伴随化学发光现象。实验研究了酸性介质、 $\text{KMnO}_4$  浓度以及  $\text{N}_2$  或  $\text{O}_2$  气氛对体系化学发光的影响, 分析了化学发光反应前后的紫外可见吸收光谱和 X-射线光电子能谱 (XPS) 的异同, 在此基础上提出化学发光反应的机理可能是酸性条件下  $\text{KMnO}_4$  被纳米金还原生成激发态  $\text{Mn(II)}^*$  而产生化学发光。

4. 实验发现不同粒径的纳米金对于 luminol -  $\text{H}_2\text{O}_2$  液相化学发光体系具有不同程度的增强作用, 其中粒径为 38 nm 的纳米金对于体系的化学发光具有最大的增强作用。利用紫外可见吸收光谱、透射电镜 (TEM) 和 X-射线光电子能谱 (XPS) 技术以及脱气实验研究化学发光反应的可能机理, 推测纳米金对该体系化学发光的增强作用可能是由于纳米金对于反应过程中自由基的生成以及后续电子转移反应具有良好的催化作用。实验研究了各种反应物的浓度、纳米金的粒径以及有机化合物对该化学发光体系的影响, 发现含有 -OH、- $\text{NH}_2$  和 -SH 的有机化合物对于 luminol -  $\text{H}_2\text{O}_2$  - 38-nm 纳米金化学发光体系具有明显的抑制作用。在此基础上, 进一步研究了 luminol -  $\text{H}_2\text{O}_2$  - 38-nm 纳米金化学发光体系测定含有 -OH、- $\text{NH}_2$  和 -SH 的有机化合物分析应用潜力, 取得了很好的结果。

5. 利用  $\text{NaBH}_4$  还原  $\text{HAuCl}_4$  合成纳米金的过程伴随微弱且不稳定的化学发光现象, 化学发光的发光体可能是反应生成的激发态金原子团簇。该体系化学发光的强度受所加入的保护试剂的影响, 可能取决于保护试剂的性质及其与激发态

金原子团簇之间的相互作用。柠檬酸根离子与金原子团簇之间的相互作用不强,因此柠檬酸钠的加入对体系化学发光没有明显影响;没食子酸、对氨基苯硫酚和巯基乙酸钠的加入会抑制化学发光的强度,可能是由于这些保护试剂具有较高的化学活性并且与金原子团簇之间有较强的相互作用;表面活性剂十二烷基磺酸钠的加入使体系的化学发光增强,可能是由于表面活性剂分子有利于激发态金原子团簇的稳定。激发态金原子团簇也可以将能量转移给共存的荧光物质如荧光素和罗丹明 B,从而得到增强的化学发光。Luminol 参与  $\text{NaBH}_4 - \text{HAuCl}_4$  的反应可以得到更强更稳定的化学发光信号,可能是由于  $\text{NaBH}_4$  与  $\text{HAuCl}_4$  反应生成了强氧化性的  $\text{Au}^{\delta+}$  物种氧化 luminol 而产生强的化学发光。

**关键词：** 纳米金 液相化学发光 能量接受体 微尺度反应平台 还原剂 催化剂  
金原子团簇 分析应用

# Gold Nanoparticles Involved Liquid Phase Chemiluminescence

## Abstract

Chemiluminescence (CL) has been intensively investigated for many years. Originally, the study of liquid phase CL was limited to molecular systems and simple molecular congeries. Recently, attentions have been paid to nanoparticle systems. However, until now, only several papers have been published on semiconductor nanoparticles involved liquid phase CL, while studies on metal nanoparticles-involved liquid phase CL have not been reported on literature.

Based on reviewing the principles and recent developments in the field of CL, and the physical and chemical properties of gold nanoparticles and their applications in analytical chemistry, this dissertation chose gold nanoparticle as a model system to explore the behavior, rule, mechanism and analytical potential of gold nanoparticles involved liquid phase CL. The main results are as follows:

1 . Light emission at  $\sim 415$  nm was observed for gold particles of diameter 2.6 and 6.0 nm dispersed in a solution containing bis (2,4,6-trichlorophenyl) oxalate and hydrogen peroxide. The light intensity was found to increase linearly with the concentration of the gold nanoparticles. The gold nanoparticles were identified as emitting species and the quantum yield was determined to be  $(2.8 \pm 0.3) \times 10^{-5}$ . The light emission is suggested to involve a sequence of steps: the oxidation reaction of bis(2,4,6-trichlorophenyl) oxalate with hydrogen peroxide yielding an energy-rich intermediate 1,2-dioxetanedione, the energy transfer from this intermediate to gold nanoparticles, and the radiative relaxation of the as-formed excited state gold nanoparticles. The observed luminescence is expected to find applications in the field of bio-analysis owing to the excellent biocompatibility and relatively high stability of gold nanoparticles.

2 . The reaction of gold nanoparticles with potassium periodate ( $\text{KIO}_4$ ) – sodium hydroxide ( $\text{NaOH}$ ) – carbonate ( $\text{Na}_2\text{CO}_3$ ) system undergoes chemiluminescence with three emission bands at 380 ~ 390 nm, 430 ~ 450 nm and 490 ~ 500 nm, respectively. It was found that the light intensity increased linearly with the concentration of the gold nanoparticles and the CL intensity increased dramatically when the citrate ions on the nanoparticle surface were replaced by  $\text{SCN}^-$ . The shape, size and oxidation state of gold nanoparticles after the chemiluminescent reaction were characterized by UV-visible absorption spectrometry, transmission electron microscope (TEM) and X-ray photoelectron spectrometry (XPS). Gold nanoparticles are supposed to play as a nanosized platform for the observed chemiluminescent reactions. The chemiluminescent mechanism has been proposed to be due to that the interaction between free  $\text{CO}_3^{\bullet-}$  and  $\text{O}_2^{\bullet-}$  radicals generated by  $\text{KIO}_4 - \text{NaOH} - \text{Na}_2\text{CO}_3$  system and the gold nanoparticles results in the formation of emissive intermediates gold (I) complexes, carbon dioxide dimers and singlet oxygen molecular pairs on the surface of the gold nanoparticles. This work is not only of great importance for gaining a better understanding of the unique optical and surface properties and chemical reactivity of nanoparticles, but also of great potential for developing new biosensing and immuno labelling technologies.

3 . It was found that potassium permanganate ( $\text{KMnO}_4$ ) could react with gold nanoparticles in strong acid medium to generate particle size-dependent chemiluminescence (CL). For gold nanoparticles with the size of 2.6 or 6 nm, the reaction was fast and could produce light emission around 640 nm, and the CL intensity was found to increase linearly with the concentration of 2.6 nm gold nanoparticles. For gold nanoparticles larger than 6 nm, no light emission was observed due to much slower reaction rate. The effects of acid medium, the concentration of  $\text{KMnO}_4$  and the presence of  $\text{N}_2$  and  $\text{O}_2$  were investigated. UV-visible absorption spectra and X-ray photoelectron spectra (XPS) before and after the CL reaction were analyzed. A CL mechanism has been proposed due to that potassium

permanganate was reduced by gold nanoparticles in strong acid medium to the excited state  $\text{Mn(II)}^*$ , yielding light emission. The results bestow new light on the size-dependent chemical reactivities of the gold nanoparticles and on nanoparticles-induced chemiluminescence. The CL reaction was supposed to be of application potential for developing new biosensing techniques and immunoassay.

4 . Gold colloids with nanoparticles of different sizes were found to enhance the chemiluminescence (CL) of luminol –  $\text{H}_2\text{O}_2$  system, and the most intensive CL signals were obtained with gold nanoparticles in diameter of 38 nm. UV-visible spectra, X-ray photoelectron spectra and transmission electron microscopy studies were carried out before and after the CL reaction to investigate the CL enhancement mechanism. The CL enhancement by gold nanoparticles of luminol –  $\text{H}_2\text{O}_2$  system was supposed to be originated from the catalysis of gold nanoparticles, which facilitated the radical generation and electron transfer processes taking place on the surface of the gold nanoparticles. The effects of the reactant concentrations, the size of the gold nanoparticles and some organic compounds were also investigated. Organic compounds containing –OH, – $\text{NH}_2$  and –SH groups were observed to inhibit the CL signal of the luminol –  $\text{H}_2\text{O}_2$  – gold colloids system, which made it applicable for the determination of such compounds with detection limits as low as  $1.7 \times 10^{-9} \sim 1.9 \times 10^{-10}$  mol/L and linear range of three orders of magnitude.

5 . Weak and unstable chemiluminescence was found during the synthesis of gold nanoparticles by reducing  $\text{HAuCl}_4$  with  $\text{NaBH}_4$ . The luminophore of this CL process was probably the as-formed excited state gold clusters. The addition of protecting reagents affected the CL intensity, which were supposed to be dependent on the properties of the protecting reagents and their interactions with the excited state gold clusters. Tri-sodium citrate showed minor effects on the CL, because the interaction between citrate ions and gold clusters was not strong. Gallic acid, *p*-aminophenanthiol and mercaptoacetic acid inhibited the CL signal, probably because of their strong interactions with the gold clusters. Sodium dodecanesulphonate the

surfactant enhanced the CL intensity probably because the excited state gold clusters could be stabilized by the surfactant molecules. The fluorophores could also enhance the CL intensity, which is likely due to that the excited state gold clusters could transfer energy to fluorophores such as fluorescein and rhodamine B, leading to CL enhancement. The most intense and stable CL signals were obtained when luminol was added to react with  $\text{NaBH}_4$  and  $\text{HAuCl}_4$ , probably because strong oxidants  $\text{Au}^{\delta+}$  species generated by the reaction between  $\text{NaBH}_4$  and  $\text{HAuCl}_4$  would oxidize luminol to generate strong CL signals. The study on the CL phenomena during the synthesis of gold nanoparticles was important for both chemiluminescence and nano-sciences.

**Keywords:** Gold Nanoparticles, Liquid Phase Chemiluminescence, Energy Acceptor, Nanosized Reaction Platform, Reductant, Catalyst, Gold Cluster, Analytical Applications