

Effect of Gold Nanoparticles on Fluorescence Properties of Hyperbranched Poly (amido amine)s

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Abstract. Hyperbranched poly(amino amine)s (HPAMAMs), synthesized by Michael addition of 1-(2-aminoethyl) piperazine (AEPZ) and methyl acrylate (MA), can emit blue fluorescence under excitation wavelength. However, the relatively weak fluorescence of HPAMAMs is still an obstacle for its practical applications. Gold is one of the most frequently used metals for fluorescence enhancement. In this research, the influence of gold nanoparticles on fluorescence property of HPAMAMs was investigated by fluorometry. It was found that gold nanoparticles (GNPs) with smaller size (< 5 nm) presented greatly enhanced emission. The GNPs with larger size (~10 nm in diameter) and definite surface plasmon absorption can quench the fluorescence of HPAMAMs.

1 Introduction

Fluorescence is rapidly becoming a leading methodology in life sciences [1] because of its versatility, potential for multiplexing, ease of use, and remarkable sensitivity. Apart from fluorophore stability, the detection limit of a fluorophore is determined by the ratio of its signal to the background emission due to unavoidable sample autofluorescence. Therefore high fluorophore brightness is a critical requirement for fluorescence detection of trace analytes, especially in the presence of any interfering background fluorescence, and a range of methods have been developed to increase the sensitivity of fluorescence detection [2]. Fluorescence amplification by metal nanostructures is a relatively new methodology that has been explored extensively over only the last decades [3]. Amplification of fluorescence is a nanoscale phenomenon which is particularly pronounced in close proximity to metal nanostructures. The phenomenon of metal induced fluorescence enhancement (MIFE) is attributed to interaction of the excited fluorophores with surface plasmon resonances in metals. The enhanced electric field around the particle increases the fluorescence intensity and quantum yield of the fluorophore [4]. This results in a strong increase of the number of emitted photons per fluorophore, and thus improved detection limits.

Gold is one of the most frequently used metals for fluorescence enhancement. Gold surfaces can resist oxidation and remain stable for many months after preparation. Importantly, gold-based substrates such as Au colloids can be produced with well-controlled and homogeneous coverage [5]. Dickson and colleagues reported a more successful method for producing gold nanoclusters with discrete size, emission, and much increased quantum yields [6], which can be utilized as a basis for ultrasensitive analytical techniques in biology and medicine [7]. Wilcoxon et al [8] reported that fluorescence occurs only when the size of the metal nanocluster is sufficiently small (< 5 nm). The luminescence maximum moves to lower energy or disappears with increased core size, and only the smaller nanodot was observed to luminesce. The luminescence from gold nanodots is thought to arise from transitions between the filled d band and sp conduction bands. Murray's group reported that for 451 nm excitation, gold clusters with 1.8 nm diameter cores and protected by monolayers of tiopronin thiolate can produce luminescence [9]. The complex with GNPs encapsulated in the interior of the polymer may generate fluorescence and enhance the fluorescence intensity of the complex associated with interband transitions between the filled 5d¹⁰ band and 6 (sp)¹ conduction band.

MIFE is a complex phenomenon. It has been investigated intensively both theoretically and experimentally, in single molecule and ensemble studies. It has been found that the degree of fluorescence enhancement is determined by many parameters. For example, it depends on the spectral overlap between the surface plasmon and the fluorophore excitation and/or emission peak. Furthermore, there is a dependence on the distance between fluorophore and metal particle. Also the medium has to be considered, as its dielectric constant and refractive index affect the properties and optical coupling of fluorophore and metal particle [10, 11]. In this research, the influence of gold nanoparticles on fluorescence property of hyperbranched poly(amido amine)s, synthesized by Michael addition of 1-(2-aminoethyl) piperazine (AEPZ) and methyl acrylate (MA), was investigated by fluorometry. These researches are beneficial to better understand the fluorescence behavior of hyperbranched polymers and meaningful to their practical applications.

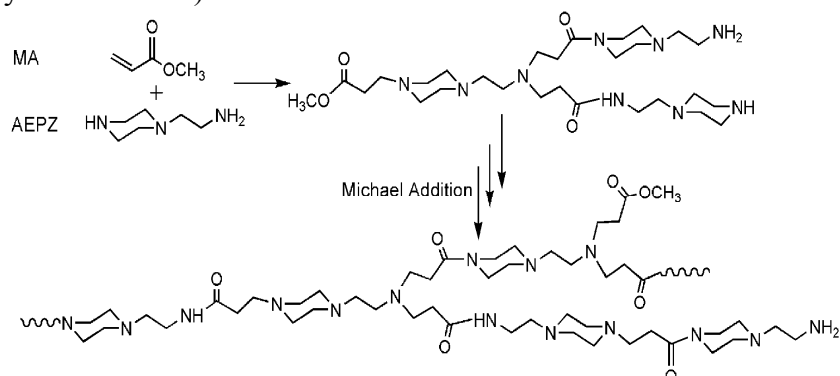
2 Experimental Section

2.1 Materials.

1-(2-aminoethyl) piperazine (AEPZ) and methyl acrylate (MA) were purchased from Sigma-Aldrich and used as received. Propylene oxide (PO) was purchased from East-China Chemical Co. and used as received. All reagents and solvents of analytical grade were purchased from commercial suppliers and used without further purification unless stated otherwise.

2.2 Synthesis of HPAMAMs

Hyperbranched poly(amidoamine)s (HPAMAMs) were synthesized by Michael addition of 1-(2-aminoethyl) piperazine (AEPZ) and methyl acrylate (MA) according to the literature procedures, as shown in Scheme 1 [12]. The resultant product was dried in vacuum for 24 h. $M_n = 1.54 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ (by GPC method).



Scheme 1. Reaction scheme for preparing fluorescent and biodegradable hyperbranched poly(amidoamine)s (HPAMAMs) from AEPZ and MA

2.3 Preparation of Gold Nanoparticles (GNPs)

The synthesis of aqueous GNPs with smaller size took reference from Huang et al [13]. The GNPs was prepared through reduction of Au with tetrakis(hydroxymethyl)phosphonium chloride (THPC, 10 μL) from hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 50 mM, 1 mL) in sodium tetraborate buffer at pH 9.2. GNPs about 10 nm in diameter were prepared through the redox reaction of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and NaBH_4 according to the literature procedures [14].

2.4 Measurement

UV/vis spectra were recorded on a 760 CRT UV/vis spectrometer (Shanghai Analytical Instrument Factory). Fluorescence measurements were performed on an LS55 luminescence spectrometer (PerkinElmer, America) using a 10-mm-path quartz cell. Unless stated otherwise, excitation and emission slit widths were set to 10 nm and 5 nm, respectively. The images of transmission electron microscopy (TEM) were obtained by a JEOL-2100 microscope. Ultrasonic mix was achieved by SK1200H (Shanghai KuDos Ultrasonic Instrument Co., Ltd.).

3 Results and Discussion

Metal nanoparticles have a variety of interesting spectroscopic, electronic, and chemical properties that arise from their small sizes and high surface-to-volume ratios [15]. Therefore, GNPs may be used to adjust the fluorescence properties of fluorescence polymer, extending potential applications of fluorescence polymer and gold nanoparticles. We investigated the enhancement of fluorescence properties of resultant polymers by GNPs. The mean diameter of GNPs used in this paper was less than 5 nm, as shown in Fig. 1.

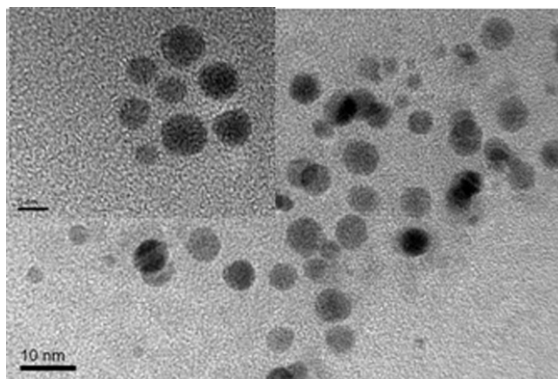


Fig. 1 TEM image of GNPs used in this study

Fig. 2 shows the absorbance spectra of pure HPAMAMs and HPAMAMs/GNPs mixture. A strong absorption band at 285 nm for two samples can be found. However, the stronger absorption band at 285 nm for HPAMAMs/GNPs mixture can be observed, as shown by B in Fig. 2. The peak positions and shapes of surface plasma resonance (SPR) of GNPs are sensitive to its particle size, therefore absorbance spectroscopy is useful for charactering metal nanoparticles [16]. A weak plasmon band around 520 nm can be found in HPAMAMs/GNPs mixture, which was attributed to their small particles size. Similar trends were observed for GNPs in previous reports [17].

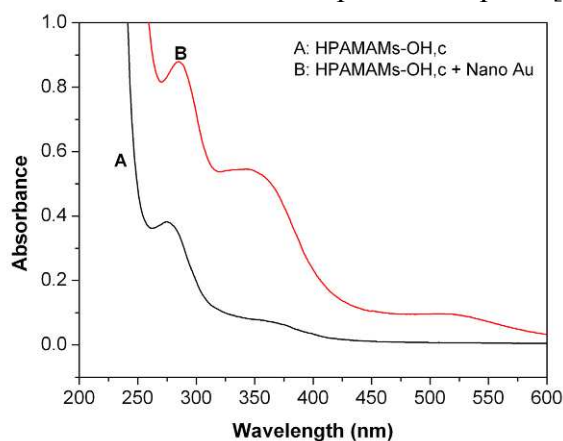


Fig. 2 UV-vis absorption spectra of pure HPAMAMs (A), HPAMAMs and GNPs mixed for 24 h (B). The concentration of HPAMAMs and GNPs are 3.25×10^{-5} and 1.25×10^{-5} mol/L. The pH value of the samples were about 7

Since the HPAMAMs and GNPs do not contain fluorescent functional groups from the classical viewpoint, exploring the source of the fluorescence should be interesting. We observed blue photoluminescence from the HPAMAMs without any treatment or functionalization. As we reported, hyperbranched poly(amido amine)s (HPAMAMs) can emit blue fluorescence under excitation wavelength. HPAMAMs exhibited an excitation band at around 225 nm and emission band at 300 nm [18]. However, after HPAMAMs were mixed with GNPs, the stronger blue photoluminescence from the solution can be observed. As shown in Fig. 3, 1.5-fold enhancement in fluorescence intensity of HPAMAMs by GNPs can be found when the concentration of HPAMAMs was fixed at 3.25×10^{-5} mol/L, while the excitation band was red-shifted from 225 nm in pure HPAMAMs to 250~350 nm and emission band was also shifted from 290 nm to 430 nm in HPAMAMs/GNPs mixture. The changes of fluorescence intensity may be attributed to the interaction of gold particles with backbone

of the HPAMAMs, which induced the conformational rearrangement of the HPAMAMs. The hyperbranched polymers with flexible nature have non-rigid plane, while the existence of GNPs in the interior of the HPAMAMs make its non-rigid plane turn to rigid, which causes the fluorescence intensity of HPAMAM rised and red shift of the emission peak [19]. Some literatures reported that fluorescence occurred only when the size of the metal nanocluster was sufficiently small (< 5 nm). The luminescence maximum moved to lower energy or disappeared with increased metal size, and only the smaller nanodot was observed to luminesce [20]. The luminescence from gold nanodots was thought to arise from transitions between the filled d band and sp conduction bands [21, 22].

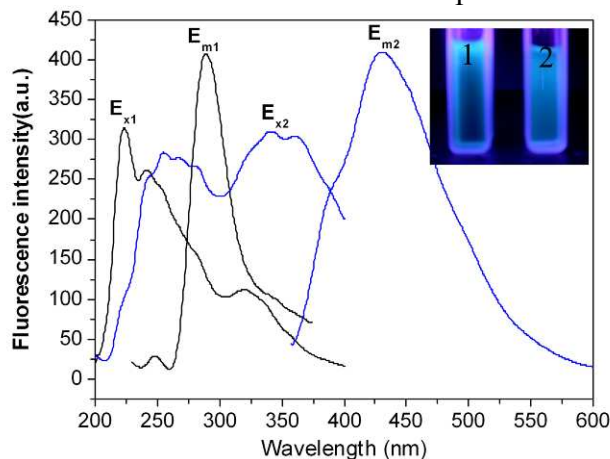


Fig. 3 Fluorescence excitation and emission spectra of HPAMAMs solution without GNPs (1) and with 1.25×10^{-5} mol/L GNPs (2) after 24 hr incubation. The concentration of HPAMAMs was 3.25×10^{-5} mol/L. The pH value of the samples was about 7

Another interesting phenomenon was that the photoluminescence spectra were dependent on GNPs concentration. Fig. 4 reveals the effect of GNPs concentration on excitation band of HPAMAMs/GNPs solutions. Going from curves A to E, the concentration of GNPs increased from 0 to 7.4×10^{-5} mol/L. The excitation band at around 225 nm decreased in intensity with increasing the concentration of GNPs in the solution. A weak broader band at 325 nm in curve A (pure HPAMAMs), in which GNPs were absent from the mixture, can be observed. However, after mixing with GNPs, the HPAMAMs/GNPs aqueous solution excited with progressively longer wavelengths from 325 nm red-shifted to 370 nm. In the pure HPAMAMs aqueous solution, the excitation intensity at 225 and 370 nm were I_{01} and I_{02} , respectively. After adding GNPs into HPAMAMs solution, the fluorescent intensity changed to be I_1 and I_2 . The plot of I_1/I_{01} and I_2/I_{02} versus different GNPs concentrations is shown in the inset of Fig. 4, the excitation intensity exhibited a good linear relationship with GNPs concentration in the mixture.

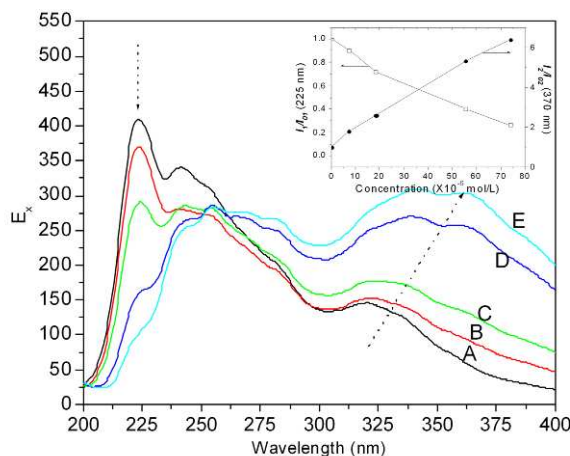


Fig. 4 The effect of GNPs concentration on excitation band of HPAMAMs, and the plot of I_1/I_{01} (225 nm) and I_2/I_{02} (370 nm) versus different GNPs concentrations (inset). The concentration of HPAMAMs was 3.25×10^{-5} mol/L and the pH value of the samples was about 7

Fig. 5A reveals the effect of GNPs concentration on emission band of HPAMAMs/GNPs solutions. Going from curves A to E, the concentration of GNPs increased from 0 to 7.4×10^{-5} mol/L. The emission band at around 300 nm decreased in intensity with increasing the GNPs concentration in the solution. Meanwhile, a new emission band at around 450 nm increased. In the pure HPAMAMs aqueous solution, the emission intensity of HPAMAMs at 290 and 430 nm were I_{01} and I_{02} , respectively. After adding GNPs into HPAMAMs solution, the fluorescent intensity would be I_1 and I_2 . The plot of I_1/I_{01} and I_2/I_{02} versus GNPs concentrations is shown in the inset of Fig. 5A, the emission intensity exhibited non-linear relationship with GNPs concentration. Even the concentration of the added GNPs into the polymer solution was as low as 7.4×10^{-6} mol/L, the emission intensity at 290 nm decreased by 0.5-fold, and a 2-fold enhancement of fluorescence intensity of the band at 430 nm can be found. Fig. 5B shows the illumination photographs of HPAMAMs aqueous solution (Fig. 5B-a) and HPAMAMs/GNPs mixture (Fig. 5B-b-e). The concentration of HPAMAMs was fixed at 5 wt% for all samples, and the concentration of GNPs varied from 7.4×10^{-6} mol/L to 7.4×10^{-5} mol/L for samples b~e. Only weak fluorescence can be observed in HPAMAMs aqueous solution without GNPs (Fig. 5B-a). However, brighter fluorescence photographs can be obtained after mixing with GNPs, which indicated the GNPs played an important role in the enhancement of fluorescence intensity.

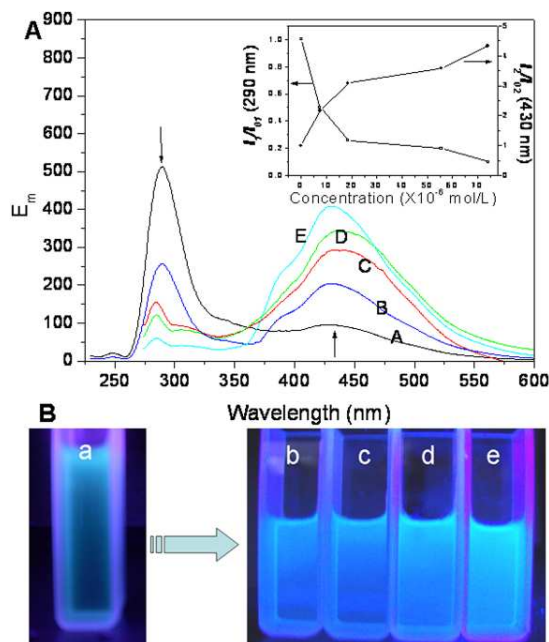


Fig. 5 The effect of GNPs concentration on emission of HPAMAMs solutions. (A): the plot of I_1/I_{01} (290 nm) and I_2/I_{02} (430 nm) versus different GNPs concentrations (inset); (B, a~e): illumination photographs of HPAMAMs aqueous solution and HPAMAMs/GNPs mixture. The concentration of HPAMAMs was fixed at 5 wt% for all samples, and the concentration of GNPs was increased from 7.4×10^{-6} mol/L to 7.4×10^{-5} mol/L for samples b~e. The pH value of the samples was about 7

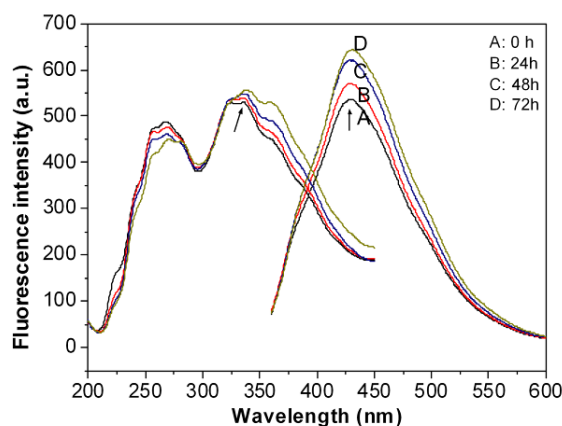
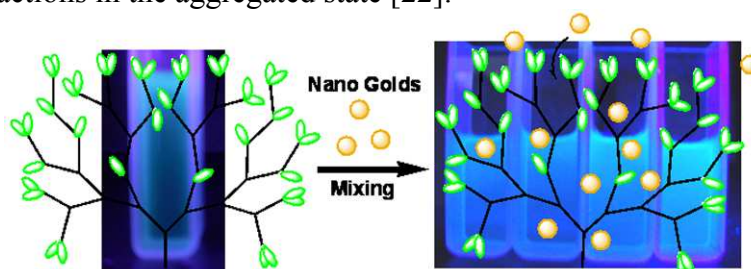


Fig. 6 Fluorescence excitation and emission spectra of HPAMAMs/GNPs solution mixed for 0, 24, 48 and 72 h. The concentrations of HPAMAMs and GNPs were 0.025 M, and 2.4×10^{-3} M, respectively. The pH value of the samples was about 7

For further investigation the effect of GNPs on fluorescence property of HPAMAMs solution, the excitation and emission bands of HPAMAMs and nano gold solutions with different incubation time were determined by fluorescence measurement. Fig. 6 shows the fluorescence intensity of HPAMAMs and nano gold solutions incubated for a period of time from 0 to 72 h under magnetic stirring. The excitation and emission intensity of HPAMAMs and nano gold solutions increased with increasing the incubation time. The excitation bands showed slight red-shift as the incubation time was prolonged, but emission bands remained the same during these process. We suppose that this phenomenon originated from the aggregation mechanisms, as shown in Scheme 2. The aggregation is driven by the van der Waals force between the nanoparticles, when the repulsive interaction is greatly reduced by complex formation on their surfaces. Then, the attractive force leads to the aggregation. Importantly, the change of the emission intensity suggested that it had a similar origin of the intramolecular interactions in the aggregated state [22].



Scheme 2. The aggregation of GNPs into hyperbranched polymer

Further support for such enhancement came from emission studies of HPAMAMs mixed with larger size gold nanoparticles. Although the origins of these enhanced emissions are still in debate, it is assumed that the unique fluorescence change is more or less related to the effects of size of gold nanoparticles (GNPs). Fig. 7 shows the contrastive fluorescence emission spectra of HPAMAMs and HPAMAMs adequately mixed with GNPs which have the mean diameter around 10 nm. It can be found that the fluorescence of HPAMAMs was quenched obviously when mixed with the GNPs. The fluorescence intensity of HPAMAMs decreased with the adding of the GNPs, as shown in the inset of Fig. 7. Gold nanoparticle can be engaged as a quencher to decrease the fluorescence intensity of fluorophores owing to fluorescence resonance energy transfer (FRET) [19]. This dynamic quenching process originated from an instantaneous exciplex formation between excited fluorescent molecules and quenchers [23], and these exciplex could not emission fluorescence or change from the original fluorescent molecules, which cause the quenching.

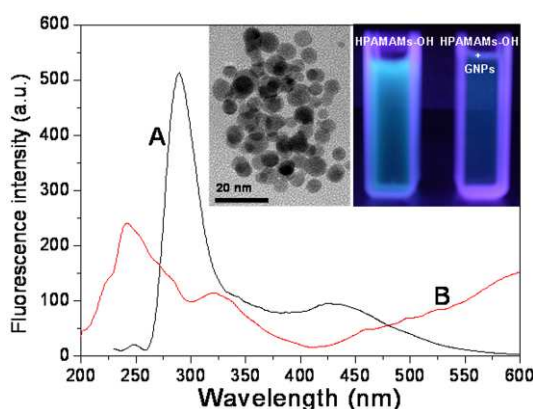


Fig. 7 The fluorescence emission spectra of HPAMAM (A) and HPAMAM/GNPs solution (B), the concentrations of HPAMAM and GNPs were 5.0×10^{-3} M, and 2.5×10^{-6} M, respectively. The pH value of the samples was about 7. The inset shows the TEM image of gold nanoparticles (GNPs, ~ 10 nm in diameter), and illumination photographs of HAMAMs and HPAMAM/GNPs aqueous solution irradiated under UV light ($\lambda = 365$ nm)

4 Conclusions

We have demonstrated the GNPs with different size exerted opposite effects on the fluorescence of HPAMAMs. The HPAMAMs and smaller GNPs mixture showed the characteristic fluorescence enhancement. Both GNPs concentration and incubation time served as the driving forces to control aggregations of GNPs with HPAMAMs resulting in emission enhancement. In the case of relatively strong binding to the surfaces of gold nanoparticles, HPAMAMs exhibited a substantial enhancement of fluorescence. It indicated that HPAMAMs/GNPs is a new fluorophore probes potentially for biological fabrication and biochemical labeling. However, the larger size GNPs with definite surface plasmon absorption can quench the fluorescence of HPAMAMs. The present work will provide a novel concept for fabricating chromophore labeled metal nanoparticles with unusual fluorescence enhancement.

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