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# Synthesis of water-soluble fluorescent gold nanoclusters

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**Abstract.** In this paper, we explored the preparation process of gold nanoclusters (AuNCs). AuNCs was synthesized by micro-reaction process and compared with the traditional one-pot strategy. The water-soluble AuNCs was prepared by reducing hydrogen tetrachloroaurate hydrate (HAuCl<sub>4</sub>) in aqueous solution with 11-mercaptoundecanoic acid (MUA) as ligand and reducing agent. The effect of NaBH<sub>4</sub> and reactant concentration ratio on the experimental results was investigated systematically, and it was found that NaBH<sub>4</sub> had little effect on the fluorescence intensity of synthesized AuNCs. When the ratio of MUA to Au<sup>3+</sup> ion concentration was 4:1, the AuNCs reached the highest fluorescence intensity. The synthesized water-soluble AuNCs were characterized by ultraviolet spectrophotometer, fluorescence spectrophotometer and high resolution transmission electron microscopy (HRTEM). The average particles of AuNCs prepared by one-pot strategy and the micro-reaction method were 1.8nm ± 0.5nm, 1.7nm ± 0.4nm, respectively. The quantum yield of AuNCs prepared by micro-reaction method was improved to 9.1% comparing with the one-pot strategy of 6.9%.

## 1. Introduction

Metal nanoclusters (NCs), a new type of fluorescent materials, have many outstanding advantages, such as small size, good photostability, easy modification, good biocompatibility, mild preparation conditions and non-toxic [1]. It shows a broad application prospect in the fields of analysis and detection [2, 3], biological imaging [4], cancer treatment [5], energy environment and science [6]. However, Compared with quantum dots and organic dyes, the quantum yield of gold nanoclusters reported is still very low, mostly less than 10%. In addition, the size uniformity of synthesized metal NCs is often poor. Polydispersity limits the application of metal NCs and makes detailed basic research on its properties more difficult. Therefore, it is particularly important to study the synthesis of monodisperse fluorescent metal NCs. [1].

The micro-reaction method is a reaction method in microchannel based on continuous flow. With narrow and regular reaction channels, small reaction space and very large specific surface area, the reactants can be fully mixed in the radial direction within millisecond range, and the process of heating and cooling can be carried out instantaneously, so as to realize precise control of the size of nanoparticles [7, 8]. However, there is few reports focusing on the application of the micro-reaction method to the synthesis of gold nanoclusters (AuNCs). In this paper, based on the remarkable advantages of the micro-reaction method, AuNCs are synthesized by the micro-reaction method and compared with traditional one-pot method.



## 2. Experimental section

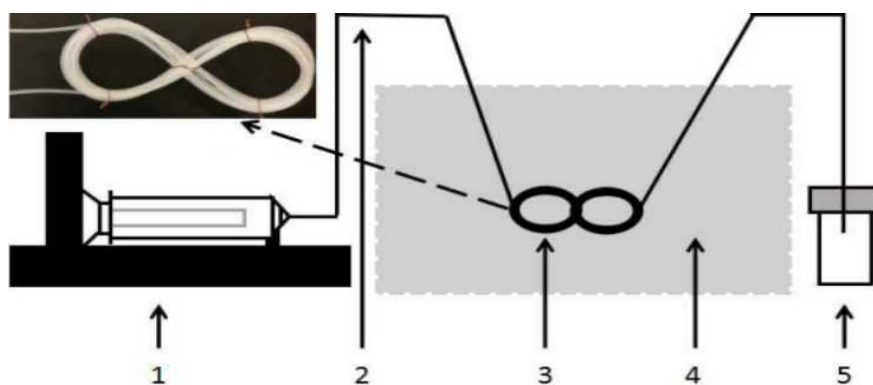
### 2.1. Reagents and Materials.

NaOH, NaBH<sub>4</sub>, Anhydrous ethanol, HCl, HNO<sub>3</sub>, 11-mercaptoundecanoic acid (MUA) and hydrogen tetrachloroaurate hydrate (HAuCl<sub>4</sub>) were purchased from Shanghai Titan Scientific, Ltd. The chemicals used in the experiment were analytical grade.

### 2.2. Luminescent MUA-AuNCs

**2.2.1. One-pot Strategy.** Washed all glassware with aqua regia and rinsed thoroughly with deionized water. 2.4 mg NaOH and 4.37 mg MUA was added to water (2ml). The solution was placed in a sonic bath for 10 minutes. Then, 5 mM HAuCl<sub>4</sub> (1.0 mL) was added to the solution and mixed for 48 hours with continuously stirring at 25 °C. Next, 1.5mL ethanol was added to the solution. The solution was centrifuged at 9450 rpm for 10 minutes. The precipitates were washed in ethanol solution (H<sub>2</sub>O/ethanol, 2:1) again. Finally, the precipitates were dissolved into water to obtain the water-soluble MUA-AuNCs [9, 10].

**2.2.2. Micro-reaction method.** Washed all glassware with aqua regia and rinsed thoroughly with deionized water. 12 mg NaOH and 21.85 mg MUA was added to water (10ml). The solution was placed in a sonic bath for 10 minutes. Then, 5 mM HAuCl<sub>4</sub> (5.0 mL) was added to the solution and mixed for 2 minutes. Then, the solution was pumped into the syringe for further use. The microreactor is shown in Fig. 1. The diameter of the capillary is 800 μm and the length is 2 m. One end of the capillary is connected with the syringe and the other end is connected with the collecting tube. The capillary was wound as figure “8” and placed in a 25 °C oil bath. The syringe was fixed to the injection pump, the injection rate was set to 251.9 μl/h, and the reactants in the collection tube remained stationary till 2 days. Finally, 1.5mL ethanol was added to the solution. The solution was centrifuged at 9450 rpm for 10 minutes. The precipitates were washed in ethanol solution (H<sub>2</sub>O/ethanol, 2:1) again. The precipitates were dissolved into water to obtain water-soluble MUA-AuNCs [7].



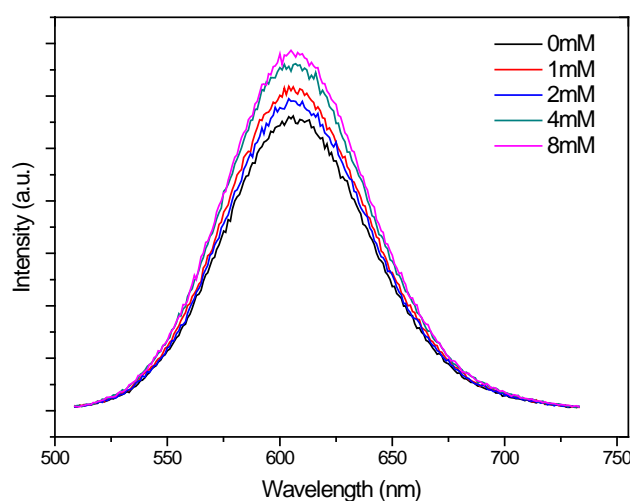
**Figure 1.** Set-up of the micro-reaction system 1.injection pump; 2.capillary; 3.microreactor; 4.heating area; 5.collector

## 3. Results and Discussions

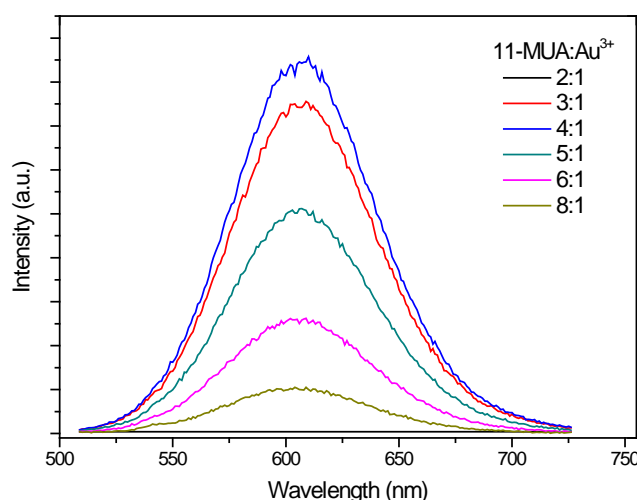
### 3.1. Preparation of MUA-AuNCs

In order to obtain monodisperse AuNCs with good stability, we chose MUA as ligand and reductant. Comparing with the use of NaBH<sub>4</sub> as a reducing agent, our method is simpler. In the early stage of the experiment, we investigated the relationship between the concentration of NaBH<sub>4</sub> and the fluorescence intensity of AuNCs. The fluorescence intensity of the NCs with NaBH<sub>4</sub> is generally stronger than that

without  $\text{NaBH}_4$ , but the fluorescence intensity is relatively close (Fig. 2). For the sake of simplifying the experimental process, we choose not to add  $\text{NaBH}_4$ . Since MUA is less soluble in aqueous solution of pH 7, in order to increase its solubility, we dissolved MUA in 30mM  $\text{NaBH}_4$  solution [9]. The fluorescence intensity of AuNCs at different concentration ratios of MUA and  $\text{Au}^{3+}$  ions was investigated. According to the ultraviolet absorption spectrum and fluorescence emission spectrum (Fig. 3), no fluorescent AuNCs are synthesized when the concentration ratio of MUA to  $\text{Au}^{3+}$  is 2:1. When the concentration ratio is higher than 2:1, the fluorescent AuNCs can be noticed. When the concentration ratio of MUA to  $\text{Au}^{3+}$  is 4:1, the AuNCs reached the highest fluorescence intensity. Such behavior shows that the ratio of MUA to  $\text{Au}^{3+}$  ions has a significant effect on the synthesis of AuNCs. Therefore, we choose concentration ratio 4:1 as the experimental parameters of our comparative experiment.



**Figure 2.** Emission spectra of AuNCs prepared at different  $\text{NaBH}_4$  concentrations.

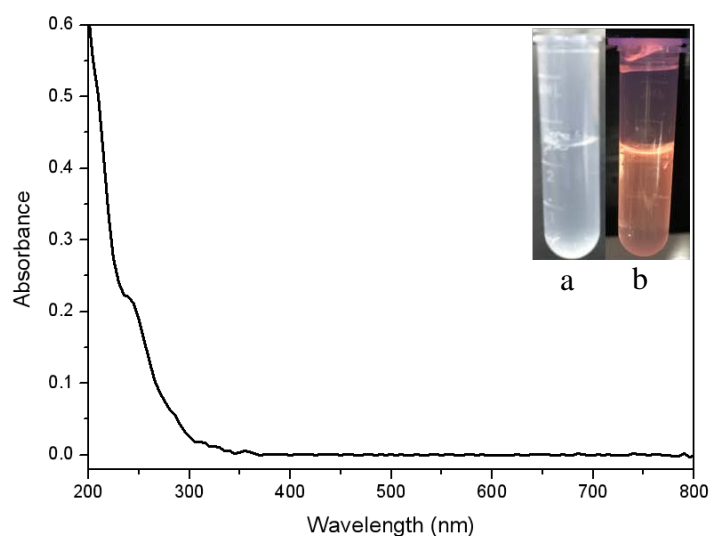


**Figure 3.** Fluorescence emission spectra (excitation at 248 nm) of AuNCs synthesized from different ratios of 11-MUA to  $\text{Au}^{3+}$ .

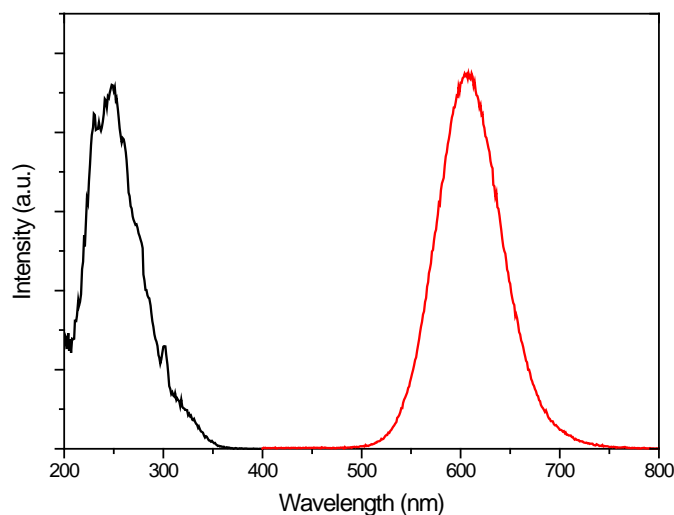
### 3.2. Characterization of AuNCs Synthesized by Ont-pot Stratergy

The AuNCs were pale white under visible light, and no fluorescence was observed when excited by ultraviolet radiation at 365 nm, and orange when excited by ultraviolet radiation at 254 nm. As shown in Fig. 4, the ultraviolet-visible absorption spectrum of the aqueous solution of AuNCs shows an absorption peak at 250 nm. The fluorescence excitation spectra of AuNCs shows that the absorption peak is at 248 nm, which is consistent with the ultraviolet-visible absorption spectra. The emission

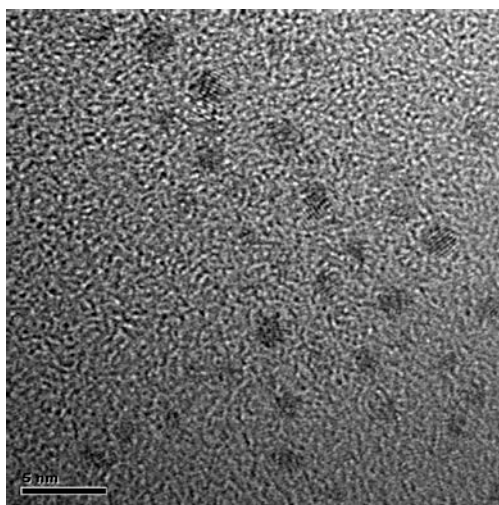
spectra of AuNCs shows that the peak is at 608 nm (Fig. 5). When the excitation wavelength is 248 nm, the fluorescence intensity is the highest. Since there is no surface plasmon peak of AuNCs near 520 nm, we believe that high purity AuNCs have been synthesized without large particles as by-products. HRTEM images show that the synthesized AuNCs have good monodispersity. The average diameter of AuNCs is  $1.8 \pm 0.5$  nm (Fig. 6). The AuNCs we synthesized are consistent with the previous literature on one-pot synthesis of AuNCs, indicating that we have successfully synthesized water-soluble monodisperse AuNCs by one-pot strategy. On the basis of one-pot process, keeping the experimental parameters such as reaction temperature, reactant concentration ratio and PH value, we improved the synthesis process by adding micro-reaction channels. We compared the synthesis results of one-pot strategy and micro-reaction method, and investigated the synthetic effect of the micro-reaction method.



**Figure 4.** Absorbance spectrum and photograph of AuNCs.



**Figure 5.** Fluorescence excitation (black line) and emission (red line) spectra of MUA-AuNCs.

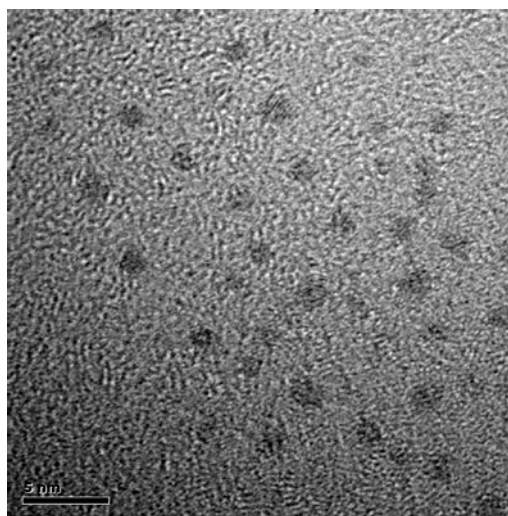


**Figure 6.** HRTEM image of AuNCs.

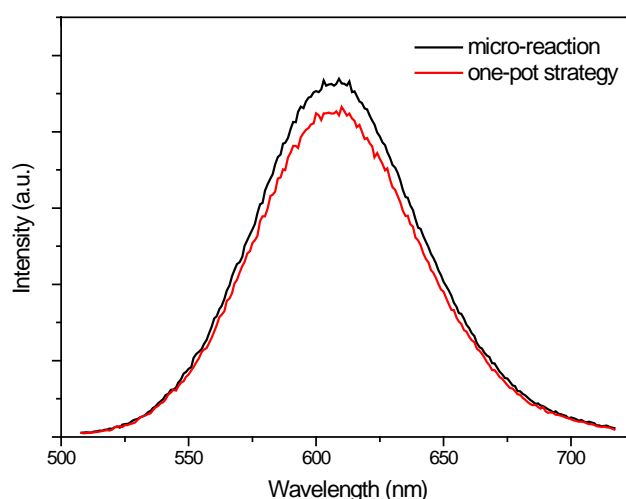
### 3.3. Characterization and Comparison of AuNCs Synthesized by Micro-reaction Method

Similar to the AuNCs synthesized by one-pot method, it is pale white in visible light, no fluorescence when excited by ultraviolet radiation at 365 nm, and orange when excited by ultraviolet radiation at 254 nm. The absorption spectrum and fluorescence excitation spectrum of AuNCs shows an absorption peak at 250 nm, the emission peak is at 608 nm. The HRTEM images show that the AuNCs have good monodispersity. The average diameter of AuNCs is  $1.7\text{ nm} \pm 0.4\text{ nm}$  (Fig. 7). We found that the absorption spectra, excitation spectra and emission spectra of AuNCs synthesized by micro-reaction process were consistent with those obtained by one-pot method. Therefore, we believe that we have successfully synthesized water-soluble monodisperse AuNCs by micro-reaction process.

To investigate the effect of micro-reaction process on the synthesis, we compared the effect of one-pot method and micro-reaction process under the same experimental parameters. We found that under the same reaction conditions, the fluorescence intensity of AuNCs synthesized by the micro-reaction process was always stronger than that by the one-pot method, as shown in Fig. 8. In addition, we characterized the QY of the reaction products. The QY of AuNCs synthesized by the micro-reaction process and the one-pot method was 9.1% and 6.9%, respectively. From the TEM diagrams of the two kinds of AuNCs, we can find that the dimensional homogeneity of gold nanoclusters synthesized by the micro-reaction process is better. As for the difference of the synthesizing effect between the two processes, on the one hand, we think that the micro-reaction channel has better mixing efficiency than the beaker method. On the other hand, the micro-reaction channel has a very large specific surface area, and heat transfer in the oil bath is very rapid, which ensure that the uniform temperature of the reactant. Therefore, comparing with the one-pot method, the micro-reaction process has more advantages in synthesizing AuNCs.



**Figure 7.** HRTEM of MUA-AuNCs synthesized by micro-reaction method.



**Figure 8.** Emission spectrum of MUA-AuNCs prepared by micro-reaction method and one-pot strategy.

#### 4. Conclusion

Water-soluble monodisperse AuNCs were successfully synthesized by one-pot method and micro-reaction process. Under the same experimental parameters, it is found that the AuNCs synthesized by micro-reaction process displays higher QY and more uniform size. The micro-reaction process has better mixing efficiency than the intermittent reaction of one-pot method. When the micro-reaction channel is immersed in the oil bath, due to its micro-reaction space and specific surface area, it can realize efficient heating and cooling process and precise control of the size and morphology of NCs.

The results in the paper show that the micro-reaction process is feasible in synthesizing AuNCs, and has advantages in improving the size uniformity and QY of NCs. When the reaction time is shorter and the reaction temperature is higher, the advantages of precise control of micro-reaction process are more obvious. The improvement of QY, the precise control of size and morphology have an important impact on their practical applications, especially in life sciences. Moreover, the precise synthesis of AuNCs is also a hot and difficult point in current research works. This paper presents a new idea for the precise synthesis of AuNCs.

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