



Historical perspective

Fluorescence enhancement for noble metal nanoclusters

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ABSTRACT

Noble metal nanoclusters have attracted great attentions in the area of fluorescence related applications due to their special properties such as low toxicity, excellent photostability and bio-compatibility. However, they still describe disadvantages for low quantum yield compared to quantum dots and organic dyes though the brightness of the fluorescence play an important role for the efficiency of the applications. Attentions have been attracted for exploring strategies to enhance the fluorescence based on the optical fundamentals through various protocols. Some methods have already been successfully proposed for obtaining relative highly fluorescent nanoclusters, which will potentially describe advantages for the application. In this review, we summarize the approach for enhancement of the fluorescence of the nanoclusters based on the modification of the properties, improvement of the synthesis process and optimization of the environment. The limitation and directions for future development of the fabrication of highly fluorescent metal nanoclusters are demonstrated.

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1. Introduction

Noble metal nanoclusters (NCs) have attracted great attentions recently due to their specific physicochemical properties that are different from conventional nanoparticles [1]. The fluorescent NCs composed of

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several to tens of atoms and the sizes are so small that the molecular like behaviors are demonstrated. Normally, they do not exhibit featured surface plasmon resonance absorption in the visible region but describe fluorescence in the visible to near-infrared region [2]. The NCs can be designed to possess large Stokes shift, [3] long lifetime, [4] good photostability, [5] living cell compatibility, [6] catalysis properties, [7] electrocatalysis [8] and photo catalytic activity, [9] etc. Among special properties for NCs, fluorescent behaviors are most attractive for the applications because it will provide avenues for designing as sensors, [10] imaging dyes, [11] photosensitizers, [12] light-emitting devices [13] with good performance. Compared to traditional fluorescent materials like organic dyes and quantum dots (QDs), they tend to describe lower toxicity and satisfied renal clearance ability [14]. However, it should be noted that the fluorescence quantum yield (QY) of most noble metal NCs are still not competitive as compared to ODs or organic dyes [15]. If the NCs are modified with brighter fluorescence, the as obtained product can be expected to be applied as more efficient materials [16]. As well as this, the enhancement process can be made used of since the analysis protocol may be fabricated based on the fluorescence change induced by the analytes [17]. One primary reason for the difficulty to obtain NCs with high QY is the limited strategies for optimization of the factors that influences their photophysical properties. Initially, it was believed the origin of fluorescence was mainly depended on the ultra-small core size that could cause the quantum effect and influence the fluorescence behaviors, which was similar to QDs [18]. As more works are contributed to this area, the roles for the protection ligand have attracted great attentions on the influence of the fluorescence [19]. Additionally, the intrinsic structure, metal composition, hydrophilic property, surface charge, environment, and other conditions may also have different effects for the fluorescence. When the relative factors that influence the fluorescence will be at the optimum state, the QY of the NCs may possibly be greatly modified. Recently, various strategies have been tried to obtain noble metal NCs with enhanced fluorescence, but the advances for the endeavor on the fluorescence enhancement hasn't be summarized yet to the best of our knowledge. Previous reports are normally focused on the broad synthesis, structures, characterization and applications of noble metal NCs [7,20–28]. In this review, we will summarize the works that have been employed to obtain brighter fluorescent metal NCs. Meanwhile, the corresponding applications of these modified metal NCs are described. Finally, some concluding remarks and outlook for research into fluorescence enhancement for the metal NCs are demonstrated for future prospect.

2. Fluorescence enhancement based on the properties

2.1. Fabrication of alloy NCs

The formation of alloy NCs has been employed as an important protocol for the improvement of the brightness of the fluorescence through changing the structures, core position and shapes by various protocols [22]. Thereafter, these changes could affect the fluorescence properties of metal NCs significantly. The doping of another metal in NCs for the enhancement of fluorescence has been reported by different papers.

The most common combination for fabrication of alloy NCs are doping gold NCs (Au NCs) with silver, which have described considerable enhancement effect. Additionally, other combination for NCs between noble metals can also be employed for the enhancement of the fluorescence. A summarization for recently work on the employment of alloy NCs for modification of fluorescence behaviors are described in Table 1. For instance, Jin has fabricated series of the phosphine-protected $\text{Ag}_x\text{Au}_{25-x}$ NCs [29]. Initially, the as prepared Au NCs describe quite low QY. After the fabrication of alloy $\text{Ag}_x\text{Au}_{25-x}$ NCs, they haven't described significant fluorescence change when $x \leq 12$. However, it is further found substituting Ag with Au in the matrix of the 25 Au atoms can significantly enhance the fluorescence of the NCs. It is proposed the atomic-level structure can only be obtained when $X = 13$, which enables the formation of highly fluorescent alloy NCs. The fluorescence QY of the as modified $\text{Ag}_{13}\text{Au}_{12}$ NCs is as high as 40.1%, which describes 200 fold enhancement compared to the $\text{Ag}_x\text{Au}_{25-x}$ NCs when $x \leq 12$. After the modification, it has been demonstrated $\text{Ag}_{13}\text{Au}_{12}$ NCs describe excellent efficiency for human cancer cell imaging though the original Au NCs are not of practical for bioimaging or related applications. As well as phosphine-ligand protected Au NCs, the introduction of Ag for fabrication of alloy NCs that can enhance the fluorescence are also available by using other template. For instance, Bovine serum albumin (BSA) and glutathione (GSH) protected Au-Ag NCs describe fluorescence enhancement compared to Au NCs though the exact number of each atom is not mentioned [30–32]. Furthermore, Cu can also be used like Ag to enhance the fluorescence of Au NCs. Recently, Kazan reported the fluorescence of Au_{38} NCs was significantly enhanced after the fabrication of $\text{Au}_{38}\text{Cu}_1$ due to the change in the electronic structure as well as the restriction of intramolecular movement for the SR units in protection ligand by the addition of copper [33].

Besides the fluorescence enhancement for Au NCs, doping Ag NCs with Au will improve the fluorescence of QY as well. Giada Soldan found doping discrete number of Au atoms in Ag NCs could not only enhance the fluorescence brightness but also the stability [34]. A 26-fold QY enhancement had been obtained by doping $\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4$ NCs with Au atoms, producing $\text{Ag}_{29-x}\text{Au}_x(\text{BDT})_{12}(\text{TPP})_4$, $x = 1-5$.

As well as the composition ratio for each metal of the alloy, it was found the fluorescence of the NCs was drastically influenced by shape. Kang has successfully designed a controllable strategy for synthesis of alloy NCs with different shapes by alloying heteroatom complexes with different ligands [35]. The shape of the spherical $[\text{Pt}_1\text{Ag}_{24}(\text{SPhMe}_2)_{18}]$ NCs could be transferred to rod-like $\text{Pt}_2\text{Au}_{10}\text{Ag}_{13}(\text{PPh}_3)_{10}\text{Br}_7$ NCs while alloying with $[\text{Au}(\text{PPh}_3)\text{Br}]$. After that, Alloy NCs with much higher QY (14.7%) was obtained. Compared to the fluorescent $\text{Pt}_1\text{Ag}_{24}$ NCs (QY = 0.1%) with spherical shape, the QY of $\text{Pt}_2\text{Au}_{10}\text{Ag}_{13}$ NCs increases about 150 times. Progress has been made for the fluorescence enhancement of NCs by the fabrication of alloy NCs, but most of the NCs are built by doping Nobel metal NCs with other noble metal element [22]. In the future, after wide investigations are contributed to this area, the combination with other common metal or metal oxide such as Zn or ZnO may also contribute to the QY enhancement for metal NCs due to the charge transfer or structure change, which may also describe more excellent application efficiency.

Table 1
The fabrication of alloy NCs for the fluorescence enhancement.

Nanoclusters	Combination	Enhancement fold	Reference
$[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_4\text{Ph})_5\text{Cl}_2]^{2+}$	$\text{Ag}_x\text{Au}_{25-x}$ ($x = 13$)	200	[29]
Au_{16} NCs@BSA	hybrid Au@Ag NCs adducts	2	[30]
GSH-Au NCs	GS-Au/Ag NCs	3.5	[32]
BSA-Au NCs	BSA-AuAg NCs	6.5	[36]
Au NCs@GSH	AgAu NCs (Ag: (Au + Ag) = 1: 20)	4–5	[37]
$\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4$	$\text{Ag}_{29-x}\text{Au}_x(\text{BDT})_{12}$ ($x = 1-5$)	26	[34]
$\text{Pt}_1\text{Ag}_{24}(\text{SPhMe}_2)_{18}$	$\text{Pt}_2\text{Au}_{10}\text{Ag}_{13}(\text{PPh}_3)_{10}\text{Br}_7$	150	[35]
$\text{Au}_{38}(2\text{-PET})_{24}$	$\text{Cu}_x\text{Au}_{38}(2\text{-PET})_{24}$ ($x = 1$)	–	[33]

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