Advances in Colloid and Interface Science 207 (2014) 164–177

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Controllable metal-enhanced fluorescence in organized films and colloidal system

Qianling Cui [a,b], Fang He [a], Lidong Li [a,*], Helmuth Möhwald [b]

[a] School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
[b] Max Planck Institute of Colloids and Interfaces, 14476 Potsdam-Golm, Germany

ARTICLE INFO

Available online 18 October 2013

Keywords:
Fluorescence
Self-assembly
Multilayers
Nanoparticles
Polyelectrolytes

ABSTRACT

In recent years, considerable efforts have been devoted to better understand the unique emission properties of fluorophores enhanced by the localized surface plasmon resonance of metal nanoparticles (NPs), due to the widespread applications of fluorescence techniques. It is demonstrated by experiment and theoretical calculation that the enhancement efficiency strongly depends on the morphology of the metal NPs, the spectral overlap between metal and fluorophores, the separation distance between them, and other factors. Among these aspects to be considered are suitable spacer material and assembling methods to control the spatial arrangement of plasmonic NPs and fluorophore with proper optical properties and interactions. In this contribution, we provide a brief overview on recent progress of metal-enhanced fluorescence in organized films and colloidal systems.

Contents

1. Introduction

Fluorescence is one of the most popular techniques for labeling, sensing and imaging in chemical, biological, medical and diagnostic fields [1–3]. The development of novel fluorescent materials has accelerated the advances in this area, such as nanotechnology-based quantum dots (QDs) [4,5], conjugated polymers [6,7], upconversion nanoparticles (UCNs) [8,9] and proteins [10]. For practical applications, fluorophores are generally required to exhibit high brightness and photostability. However, common fluorophores always have small extinction coefficient, low quantum yield, bleaching and/or blinking phenomena, especially for the newly-developed fluorescent probes mentioned above. The metal-enhanced fluorescence (MEF) may provide

---

* Corresponding author at: School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China. Tel.: +86 10 82377202; fax: +86 10 82375712.
E-mail address: lidong@mater.ustb.edu.cn (L. Li).

0001-8686/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cis.2013.10.011

a promising way to address these problems, as it was demonstrated that the optical properties of fluorophores can be modified by adjacent metallic nanostructures [11,12]. Since 1980s when the MEF was confirmed by experiment [13,14], the exploration of fundamental theories and fabrication of functional materials based on MEF have received increasing attentions [15–19].

The interesting MEF phenomenon relates to the unique localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs), which is caused by the collective oscillations of the conduction-band electrons. Upon light radiation, the local electromagnetic field can be concentrated strongly in the vicinity of a metallic surface. If a fluorophore is placed in close proximity to this plasmonic nanostructure, its spectral properties can be altered by both the excitation and emission modifications [20]. First, its excitation rate can be increased by the enhanced local field resulting from exciting the LSPR. Second, its nonradiative decay is accelerated by the excitation-plasmon interaction, leading to increase in quantum yield and decrease in fluorescence lifetime. The high excitation and emission rates are important for imaging or detecting trace amounts of targeted species, especially for single-molecule fluorescence detection [18,19,21].

To realize MEF, the fluorophore is needed to be close enough to the plasmonic nanostructure, since the field enhancement decays nearly exponentially with distance from the metallic surface. But if the fluorophore is too close (less than 5 nm) or even directly attached to the surface, its fluorescence would be quenched significantly due to the nonradiative decay through energy and/or charge transfer to the metal [20]. To avoid fluorescence quenching, a spacer interlayer with appropriate thickness (5–30 nm in general) is usually desired to separate fluorophore and metal nanostructure, as well as a linker to bridge them. As a result, a common MEF system is always composed of three components, including the metal nanostructure, fluorophore and a spacer layer. It has been demonstrated by experiment and theoretical calculations that the degree of fluorescence enhancement is related to the metal species, size and geometry of metal nanostructures [22,23], orientation of fluorophore towards the metallic surface [24,25], distance between metal and fluorophore [26–28], their spectral overlap [29–32], and excitation polarization [33,34]. To realize the optimal MEF effect and to better understand the mechanism, these factors have to be considered and tailored carefully.

Up to now, various metal species with MEF functions have been reported, including silver, gold, aluminum [35], copper [36], zinc [37], chromium [38], iron [39], and rhodium [40]. Among them, silver and gold nanocrystals are the most widely used amplifying materials, due to their LSPR bands in the visible and near-infrared spectra regions. Silver has a high scattering and enhancement efficiency [41–43], whereas gold possesses chemical inertness and stability, biocompatibility, facile modification or conjugation to biomolecules [44,45]. The metallic surfaces and nanostructures with various morphologies can be fabricated by wet chemical methods and advanced lithography techniques such as electron beam lithography (EBL) [46] and nanoimprint lithography [47–49]. Generally, stronger field enhancement is always found for anisotropic plasmonic NPs with sharper tips, edges and corners. For instance, fluorescence enhancements of up to several thousand times were measured for gold nanorods (AuNRs) [50] and gold nanoshells (AuNSs) [51]. The choice of metal nanostructures and fluorophores depends on the demands of particular applications.

Another important issue in the fabrication of MEF systems is the establishment of an appropriate spacer layer with suitable materials to separate and connect fluorophore and metal NPs. It requires the spacer materials to be reproducible, nonabsorbing, smooth and compact, and with the ability to vary the thickness in the nanometer range. Up to date, a variety of materials have been employed to finely tune the fluorophore–metal distance, including silica, synthetic polymers, DNA, proteins and others. How to control the spatial positioning of metal NPs and fluorophore is also a critical challenge, which has been addressed by self-assembling techniques such as layer-by-layer (LbL) assembly, core-shell particles, and bioconjugation. In this contribution, we review the establishment of a MEF system, with special emphasis of the construction of a spacer layer, including those in organized films and in colloidal systems. The features of each spacer material including advantages and drawbacks are summarized in Table 1. For some special cases where fluorescence enhancement was also observed without presence of spacer layer [52–57], they are not included in our discussion here.

2. Metal-enhanced fluorescence in organized films

The majority of the current MEF works have been performed on planar surfaces, and relatively high enhancement factors have been observed, up to 3 orders of magnitude [49,50,58–60]. The improvement of the emission properties of fluorophore-containing thin films can be exploited to develop novel fluorescence-based devices such as sensors, waveguides, light-emitting devices, and solar cells [30,61–63]. Physical and chemical methods have been utilized to fabricate plasmonic nanostructures as the magnifying substrate, including thermal evaporation [19], lithography [46], chemical deposition, electrochemical deposition

Table 1
Summary of major advantages and drawbacks of different spacer materials in MEF platforms.

	Spacer materials	Advantages	Drawbacks	References
MEF in organized films	Dielectric film	Optical transparency, easy preparation, stability	Rigid material, limitation in distance-control	[47,67–75]
	Langmuir-Blodgett films	Ultrathin films down to molecular level, precise control on molecular orientation	Sophisticated preparation, low stability	[28,76–79]
	Polymeric matrix	Easy fabrication,	Difficult to calculate the metal-dye distance	[41,46,75,80–84]
	Layer-by-layer multilayer films	precise control of architecture, composition and thickness, providing binding sites, stimuli-responsiveness	Limited in choice of polyelectrolytes and charged fluorophores	[26,27,85–110]
	Polymeric micelles on films	Easy dispersion of both the hydrophobic and hydrophilic fluorophores	Additional synthesis of copolymers	[111–113]
	Biomolecular spacer layer, including proteins, DNA, and RNA etc.	Excellent biocompatibility and non-immunogenicity, providing binding sites and specific recognition affinity	Strict preservation condition, high cost	[29,51,114–136]
MEF in colloidal system	Silica	Good transparency, easy modification, chemical inertness, low toxicity, thermal stability, low cost	Rigid material	[57,137–144]
	Polymers, including polymeric matrix, linear polymer chain, Layer-by-layer multilayer films	Variety, easy modification, stimuli-responsiveness	Difficult to calculate the metal-dye distance	[166,180–193]
	DNA sequences	Precise control on distance	Strict experimental condition, elaborate purification, high cost	[22,194–199]
	Proteins	Excellent biocompatibility and non-immunogenicity, specific recognition	Limitation in distance-control	[200–209]