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Plasmonic Ag/SiO$_2$ composite nanoparticles doped with europium chelate and their metal enhanced fluorescence

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ABSTRACT

We report silver nanostructure-enhanced fluorescence of a europium (Eu) chelate, BHHCT-Eu-DPBT, which was covalently bound in Ag/SiO$_2$ nanocomposites. This design enhances the europium signal intensity by more than one order of magnitude, and accelerates the decay time from 0.3 ms down to 60 microseconds, at low excitation conditions. These nanocomposites were bright enough to be observed in time-gated fluorescence microscopy under 365 nm LED excitation. The increased brightness and reduced lifetime of such fluorescent core-shell nanocomposites will enhance their applicability for ultrasensitive bioassays and bioimaging, especially with time-gating.

Keywords: Ag/SiO$_2$ nanocomposites; metal-enhanced fluorescence; time-gated bioimaging; Eu chelate; single particle detection

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1. INTRODUCTION

Fluorescence is an important tool used in biochemical research, drug discovery, and clinical diagnostics. It has become one of the dominant methods in DNA sequencing, genomics and proteomics. One of the fundamental challenges in these applications is to lower the limit of biomolecular detection. The feasibility of fluorophore detection is usually limited by its quantum yield, autofluorescence of the sample and/or photostability of fluorophores.

A large number of investigations have been reported recently using metallic nanostructures to favourably modify the properties of close fluorophores and to alleviate some of their classical photophysical constraints. The nanoscale fluorophore-metal interactions give rise to the process known as metal-enhanced fluorescence (MEF)\(^1\)\(^-\)\(^4\). The MEF is due to excited fluorophores interacting with surface plasmon resonances in metals, and this effect is particularly well pronounced in metal nanostructures. The MEF has been shown to produce desirable effects such as increased quantum yield of fluorophores, their decreased lifetimes, increased photostability, and potential for improved energy transfer\(^1\). At present MEF is most frequently obtained with Ag nanostructures\(^2\)\(^-\)\(^7\),\(^11\)\(^-\)\(^12\) where the highest fluorescence enhancement factors (in the range of thousands) have been reported and sometimes by using gold\(^8\)\(^-\)\(^9\) or aluminium\(^10\)\(^-\)\(^11\). Various nanostructure shapes have been examined in the context of MEF, including silver island film (SiFs)\(^2\), silver colloids\(^1\)\(^,\)^\(^4\), silver nanorods\(^3\), silver triangles\(^4\), and silver fractal-like nanostructures\(^5\). Recent studies of MEF have been performed on a range of fluorophore-doped metal (i.e. silver or gold)-core/silica-shell nanocomposites\(^13\)\(^-\)\(^17\) due to their unique advantages compared to simpler metal nanostructures previously reported. Firstly, silica is chemically inert and it does not affect redox reactions at the core surface. Secondly, the silica shell can also be used to modulate the metal core-fluorophore distance which is critically important for fluorescence enhancement. Finally, such core-shell nanocomposites can be further functionalized with ease, and this facilitates their utilization in bioassays and bioimaging.

In the present work, we choose silver for the metal core and Eu chelates for fluorophores to set up a new fluorophore-doped Ag/SiO\(_2\) nanocomposite system. This choice was based on the following reasons. Silver nanoparticles have more favourable plasmon resonance characteristics than gold. The plasmon resonance in silver occurs in the visible (the position of the band is typically around 400 nm), and it is set well apart from the band-to-band transition energy, which is not the case for gold\(^18\). Furthermore, the silver plasmon band is narrower, and silver scattering efficiency is much larger than that of gold for the same nanoparticle size. This is preferable for MEF since such scattering from the metal nanoparticles normally promotes fluorescence enhancement\(^19\). With respect to the Eu chelates, they has been chosen to take advantage of their unusual chemical and spectroscopic characteristics compared with conventional organic fluorescence dyes, such as a large Stokes shift and ion-specific emission spectra\(^20\). The lanthanide chelates are gaining widespread acceptance in fluorescence labeling as a result of expanding applications in a variety of bioanalytical assays, in diagnostics, sensing and in imaging, especially with time-gating that offers exceptionally high background rejection\(^21\)\(^-\)\(^24\). However all lanthanide-based fluorophores are relatively weak compared to other fluorophores such as traditional dyes or quantum dots. MEF is one of the strategies available to circumvent this problem. In this context it is worth noting the overlap between the absorption band (~350 nm–450 nm) of Eu chelate used in this study, BHHCT-Eu-DPBT (see Figure 1a), and the silver plasmon band (~420 nm–480 nm) is high and this leads to the expectation that for these fluorophores the MEF effect induced by Ag nanoparticles will be strong.

The aim of this work is to explore and optimize the fluorescence enhancement of BHHCT-Eu-DPBT doped into Ag-core/silica-shell nanocomposites, where both the silver-fluorophore distance and the Ag-core size are adjusted to optimize the fluorescence enhancement. This is achieved in the following way. Firstly, the thickness of the first silica shell is controlled by using different amount of tetraethyl orthosilicate (TEOS) which is able hydrolyze to generate silica sols on the surfaces of silver nanoparticles. To facilitate this reaction ammonia is added as a catalyst for hydrolysis and condensation of TEOS. Once the core has been covered with the first shell, the APS-linked BHHCT-Eu-DPBT (APS-BHHCT-Eu-DPBT) is then covalently linked to a second, thinner exterior silica shell (see Figure 1b). Such system of layers makes it possible to systematically investigate the fluorescence enhancement of Eu chelates by Ag. Furthermore, the Ag-core size is varied by the growth of citrate-reduced silver colloids using metal deposition, which is an effective
way of modifying the particle size. The fluorescence intensity enhancement from BHHCT-Eu-DPBT is also optimized by adjusting the Ag core size.

2. EXPERIMENTAL SECTION

2.1 Materials

The following materials were purchased from Sigma-Aldrich and used as received: silver nitrate (AgNO₃), trisodium citrate, TEOS, sodium cyanide, ethanol, concentrated H₂SO₄. 30% H₂O₂ was obtained from VWR. APS-BHHCT-Eu-DPBT was prepared as previously reported²⁵. Glass microscope slides were obtained from Fisher Scientific. Nanopure water (>18.0 MΩ) purified using the Millipore Milli-Q gradient system, was used in all the experiments.

2.2 Synthesis of Ag colloids

Silver nanoparticle colloids were prepared by reduction of silver nitrate with trisodium citrate¹⁴, ²⁶. Freshly prepared 10 mL of 1% trisodium citrate was respectively added within 2 min into 490 mL of boiling aqueous solution containing 23 mg and 90 mg of AgNO₃ under vigorous stirring. After boiling for 1 hour, the reaction solution was cooled to room temperature. The as-prepared silver colloid solution was centrifuged at 500 rpm for 1 hour to remove the larger colloids. In this way, silver colloids with an average size of 81 nm and 52 nm were obtained. Smaller silver colloids were prepared from above silver colloids with an average size of 52 nm by using the following procedure. 20mL of initial silver colloids was added to 380 mL of boiling Nanopure water followed by the addition of 90 mg of AgNO₃. Subsequently, 10 mL of 1% trisodium citrate was added dropwise to the suspension which was kept boiling for 30 min. This procedure leads to the formation of colloids with different silver core sizes. After cooling to room temperature, the final suspension was firstly centrifuged at 2000 rpm for 1 hour to separate larger Ag colloids followed by the second-round centrifugation of supernatant at 5000 rpm for 10 min to obtain smaller silver colloids. In this way, ~33 nm silver colloids were obtained and used for further experiments.

2.3 Synthesis of BHHCT-Eu-DPBT-doped Ag/SiO₂ nanocomposites

Ag/SiO₂ nanocomposites were prepared using a method reported by Liu et al²⁷ with some modifications. Under vigorous stirring, 50 mL of the silver colloids solution was mixed with 200 mL of ethanol followed by the addition of 4 mL of 30% ammonium hydroxide. After alkaline initiation, different amounts (2.5, 5 or 10 mL) of 10mM TEOS ethanol solution were added dropwise to the suspension. The reaction was stirred at room temperature for 24 hours. Each suspension of silica-coated silver colloids was centrifuged and washed 3 times with ethanol, followed by resuspension in 50 mL ethanol. The thickness of the silica shell was determined from TEM images and varied from ~10 nm to ~70 nm. The subsequent covalent conjugation of BHHCT-Eu-DPBT with such Ag/SiO₂ nanocomposites was achieved by using the following method. Typically, 500 μL of 2 mg/mL APS-BHHCT-Eu-DPBT toluene solution was added dropwise to 10 mL of Ag/SiO₂ ethanol solution under vigorous stirring followed by the addition of 0.24 mL of 30% ammonium hydroxide. After stirring for 20 minutes, 300 μL of 10 mM TEOS ethanol solution was added dropwise into the suspension to form the second silica shell. The reaction was allowed to continue for 24 hour at room temperature (see Figure 1b). The Eu chelate-doped Ag/SiO₂ nanocomposites were centrifuged and washed 3 times with ethanol to remove excessive APS-BHHCT-Eu-DPBT, followed by resuspension in 5 mL ethanol. Measurements were performed on these stock suspensions.

2.4 Preparation of BHHCT-Eu-DPBT-doped hollow silica nanoshells

BHHCT-Eu-DPBT-doped hollow silica nanoshells were prepared from the corresponding dye-doped Ag/SiO₂ nanocomposites by using the following strategy. 2 mL of 0.1M sodium cyanide solution was added to 1 mL of BHHCT-Eu-DPBT-doped Ag/SiO₂ nanocomposites with gentle stirring overnight to ensure complete etching of silver cores from those nanocomposites. The resulting hollow silica nanoshells were centrifuged and washed 3 times with ethanol, followed by resuspension in 1 mL ethanol. Since the Eu chelates were covalently doped in the second silica layer, the etching of silver core with cyanide ions did not cause the leakage of the chelates from the silica layer. This procedure permits the same amount of the chelates to be excited with and without silver cores, allowing more precise evaluation of the effect of silver nanoparticles than other methods by using pure silica nanoparticles as reference.
2.5 Characterization

The absorption spectra of Ag/SiO₂ nanocomposites and hollow silica nanoshells in the solution were measured using a Cary spectrophotometer (Cary 5000 UV-Vis-NIR, Varian Inc.). Transmission Electron microscopy (TEM) images were taken on a PHILIPS CM10 system at an accelerating voltage of 100 kV. The samples were prepared by placing a drop of dilute ethanol dispersion of the nanocomposites and nanoshells on the surface of a copper grid. Scanning electron microscopy (SEM) images were taken by using a JEOL-JEM-6480 LA at an accelerating voltage of 200 kV. Fluorescence spectra of samples in the solution were obtained using a Fluorolog-Tau-3 system with 450W Xe lamp excitation. The spectral width was set to 8 nm. The emission spectra were excited at 365 nm and recorded over a range of 500-670 nm. Fluorescence lifetime was measured using a purpose-built UV epi-fluorescence microscopy system (×10 objective; dichroic beam splitter (Zeiss, FT395)). A high-power UV LED (NCCU033A; Nichia Corp. Japan) with ~250 mW power at 365 nm (Δλ = 10nm) was used for excitation. In this work the UV LED was operated in a pulsed mode (1 kHz, 100 μs, 10% duty cycle). In the lifetime measurements, a pair of filters (excitation band pass filter FF01-355/40-25 and emission bandpass filter FF01-607/36-25 BP, from Semrock, http://www.semrock.com/) was employed to suppress the long decay time noise generated from the UV LED. A silicon photomultiplier (SPMT) detector (SPMMini100, SensL, www.sensl.com) was positioned after the eyepiece, so that the long lifetime luminescence could be recorded as previously described. The values of lifetime were derived by a bi-exponential curve fitting (Origin 8.0 software) with the residual error function χ² value of less than 1.0. For the fluorescence imaging measurements, the glass coverslips were first soaked in a 4:1 (v/v) mixture of concentrated H₂SO₄ and 30% H₂O₂ overnight, extensively rinsed with water, sonicated in absolute ethanol for 2 min, dried in air. A dilute solution of the sample suspensions was dispersed on the precleared coverslips. All measurements were performed using a time-gated UV epi-fluorescence microscopy system. The images of samples were recorded using a NIS-Elements BR 300 CCD camera (Nikon Instruments Inc. USA) at 2 s per frame. The imaging was performed using a × 60 objective and the time-gating was achieved by using mechanical chopper (C995 Optical Chopper from Terahertz Technologies) operating at 2.5 kHz and positioned before CCD camera. This chopper was also acting as a trigger for the pulsed UV LED. The collected colour images were analyzed using only red channel whose spectral width overlaps with the 614 nm emission of Eu chelates. All measurements were performed in the dark at room temperature.

3. RESULTS AND DISCUSSION

The typical TEM images show as-prepared Ag/SiO₂ core-shell nanostructure with a dark contrast silver core and a light contrast silica shell. These verified the presence of the silica shell and the Ag core and provided information about their respective sizes, (see Figure 2). The silica shell thickness used here gave average metal-fluorophore distances of 12 nm, 25 nm and 57 nm. In addition, as-prepared Ag colloids with different sizes were used as Ag cores with average diameters of 33 nm, 52 nm and 81 nm, as measured in the Ag/SiO₂ system. It is worth noting that 200 nm and 1000 nm long rod-shaped particles have also been observed, however, the number of rods is very low, less than 1% of the total number of particles.

Figure 3a shows the absorption spectra of the citrate-protected silver colloids and Ag/SiO₂ nanostructures with different silica shell thickness measured by using UV-visible spectroscopy. Before coating, the Ag colloids had a characteristic surface plasmon peak at ~ 425 nm. As the shell thickness is increased, there is a red shift to ~450 nm in the position of the absorption maximum, due to the increase in the refractive index of silica around the particles. When the silica shell is sufficiently large, scattering becomes significant, resulting in a strong increase in the absorbance at shorter wavelengths. This effect promotes a blue shift of the surface plasmon band up to ~432 nm and a weakening of its apparent intensity²⁸. The absorption spectra of Ag/SiO₂ nanostructures with different Ag core sizes are displayed in Figure 3b. The surface plasmon absorption peak at ~450 nm wavelengths was observed with Ag core of ~33 nm. When the size of the silver core is increased, the plasmon absorption peak shifts towards longer wavelengths up to 484 nm. This could be attributed to the following reason: the formation of larger Ag colloids will result in a red shift of their plasmon absorption peak²⁶.
In order to evaluate the effects of MEF on BHHCT-Eu-DPBT in this Ag/SiO₂ system, the corresponding “control” fluorophore-doped hollow silica nanoshells were also prepared by using the etching process where the metallic silver is oxidized to Ag(CN)²⁻ by cyanide in the presence of air, according to

$$4\text{Ag} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ag(CN)}^2^- + 4\text{OH}^-$$

This etching process ultimately leads to the formation of a hollow silica shell, as has been shown for the same reaction on silica-coated Au nanoparticles. Note that the dissolution of the core requires the transport through the silica shell of both molecular oxygen and cyanide ions, and for complete dissolution outward diffusion of silver cyanide complex anions. The decrease in the absorption of the light is shown (see Fig. 3c) as the solution changes from turbid yellow to colorless and essentially transparent. The inset in Figure 3c provides another evidence for the effectiveness of such etching process where Ag cores have been completely removed from the interiors in ~1 day to leave behind silica nanoshells with fully intact wall structures.

![Figure 1. Schematic structure of europium chelate, BHHCT-Eu-DPBT (a) and steps required in the formation of BHHCT-Eu-DPBT-doped Ag/SiO₂ nanocomposites (b).](image1)

![Figure 2. TEM images of Ag/SiO₂ nanocomposites with different thickness of silica shells (upper panel, from left to right: ~12 nm, ~25 nm and ~57 nm) and Ag-core sizes (lower panel, from left to right: ~33 nm, ~52 nm and ~81 nm).](image2)
Now we discuss the first of our key results, the demonstration of fluorescence enhancement of BHHCT-Eu DPBT by tuning the metal-fluorophore distance and Ag-core size. The typical emission spectra of BHHCT-Eu-DPBT in Ag/SiO$_2$ nanocomposites where silica shell is ~25 nm and Ag core is ~52 nm, as well as the reference control without Ag core are presented in Figure 4. Fluorescence enhancement for all samples were calculated and shown in Table 1 and Table 2. We checked that in such nanocomposites the spectral shape of the emission is unchanged compared to Eu in solution, with the emission maximum typical of Eu$^{3+}$ centered around 614 nm. For the samples with different SiO$_2$ shell thickness, a ~10.7-fold increase for the silica shell thickness of ~12 nm was obtained compared to the sample without the silver core. When the silica shell thickness was increased to ~25 nm, the optimal fluorescence enhancement of ~9.5 fold was observed. When this thickness reached up to ~57 nm, a slight decrease (~4.3 fold) in the fluorescence enhancement occurred (see Table 1). It’s also worth noting that the fluorescence enhancement factors at shorter wavelengths of 580 nm and 589 nm were relatively higher compared to that 614 nm, with a marked decrease observed at 652 nm. This is consistent with the fact that a relatively stronger MEF effect is observed for wavelengths closer to the plasmon resonance for the silver nanoparticles. Furthermore, we also established the effects of Ag-core size on the fluorescence enhancement induced by metal nanostructures near fluorophores. In order to quantify this effect, we adjusted the size of Ag cores in Ag/SiO$_2$ nanocomposites from ~20 nm to ~100 nm. By comparing the sample with different Ag-core sizes with the corresponding reference control, we obtained the different fluorescence enhancement extent (see Table 2). The enhancement at 614 nm is slightly increased (~2.0 fold) by Ag/SiO$_2$ nanocomposites with the Ag core of ~33 nm compared to the reference sample without the Ag core. The optimal fluorescence enhancement of ~10.7 fold occurred with the Ag core of ~52 nm. Further increase in the Ag-core size caused a slight decrease in the fluorescence enhancement. A ~8.4 fold increase in fluorescence intensity was observed with the Ag core of ~81 nm.

Figure 4. Luminescence intensities observed from BHHCT-Eu-DPBT-doped Ag/SiO$_2$ nanocomposites with ~25 nm silica shell and ~52 nm Ag-core size (solid line) and nanoshells without Ag core (dashed line).
For a more complete characterization of the effect of Ag/SiO$_2$ nanocomposites on the fluorescence enhancement we carried out the measurements of fluorescence lifetimes. As discussed in the literature,$^{30-31}$ metal enhanced fluorescence is characterized by an increase in the quantum yield and a decrease in the lifetime of a fluorophore located in the proximity of the metallic nanostructures. Fluorescence decay curves were acquired (see Fig. 5) for samples with and without Ag cores, and results show that Ag/SiO$_2$ nanocomposites showed a shorter lifetime compared to the corresponding hollow silica nanoshells (see Table 3 and 4). A $\sim$3.5-fold decrease in the lifetime of BHHCT-Eu-DPBT (from 212 µs to 60 µs)
was obtained by optimizing the metal-fluorophore distance and Ag-core size (silica shell: ~12 nm and Ag core: ~52 nm). The lifetime results make it possible to individually investigate the impact of silver nanostructures on the excitation and emission enhancements. These two contributors are important because the enhancement of fluorescence observed close to the nanostructured silver is a result of two effects: an increase of a local electromagnetic field near silver nanoparticles, leading to increased excitation rate of fluorophores and an increase of the radiative decay rate ($\Gamma$) of fluorophores close to metal nanostructures, reflected both in the fluorescence lifetime and quantum yield. The local electromagnetic field enhancement produces a higher excitation rate but it does not change the lifetime of the fluorophore; this effect is referred as excitation enhancement ($E_{\text{ex}}$). The second effect is referred as emission enhancement ($E_{\text{em}}$), increasing the quantum yield and reducing the lifetime of the fluorophore. Results shown in Figure 4 and Figure 5 are in accordance with these arguments. The radiative decay rate modification of BHHCT-Eu-DPBT in close proximity to the silver nanostructures is consistent with the previous reports on the MEF phenomenon and is due to the proximity of the fluorophores to the silver nanostructures.

Table 3. Fluorescence intensity decay analysis. $t_{\text{SiO}_2}$ denotes thickness of the silica shell, 1,2 denotes decay times of the two lifetime components, $\tau$ is the average lifetime.

<table>
<thead>
<tr>
<th>Eu-BHHCT-DBPT in the solution</th>
<th>$t_{\text{SiO}_2}$ (nm)</th>
<th>$\tau_1$ (µs)</th>
<th>$\tau_2$ (µs)</th>
<th>$\tau$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu-BHHCT-DBPT-doped hollow silica nanoshell</td>
<td>-</td>
<td>306±4</td>
<td>33±2</td>
<td>301±3</td>
</tr>
<tr>
<td>Eu-BHHCT-DBPT-doped</td>
<td>~12</td>
<td>216±3</td>
<td>32±2</td>
<td>212±2</td>
</tr>
<tr>
<td>Ag/SiO$_2$ nanostructures with</td>
<td>~25</td>
<td>104±4</td>
<td>28±1</td>
<td>101±2</td>
</tr>
<tr>
<td>fixed Ag-core size of ~52 nm</td>
<td>~57</td>
<td>164±3</td>
<td>36±3</td>
<td>161±3</td>
</tr>
</tbody>
</table>

Table 4. Fluorescence intensity decay analysis. $D_{\text{Ag-core}}$ denotes the diameter of Ag core, 1,2 denotes decay times of the two lifetime components, $\tau$ is the average lifetime.

<table>
<thead>
<tr>
<th>Eu-BHHCT-DBPT in the solution</th>
<th>$D_{\text{Ag-core}}$ (nm)</th>
<th>$\tau_1$ (µs)</th>
<th>$\tau_2$ (µs)</th>
<th>$\tau$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu-BHHCT-DBPT-doped hollow silica nanoshell</td>
<td>0</td>
<td>216±3</td>
<td>32±2</td>
<td>212±2</td>
</tr>
<tr>
<td>Eu-BHHCT-DBPT-doped</td>
<td>~33</td>
<td>187±4</td>
<td>3±1</td>
<td>185±3</td>
</tr>
<tr>
<td>Ag/SiO$_2$ nanostructures with</td>
<td>~52</td>
<td>60±4</td>
<td>5±1</td>
<td>60±2</td>
</tr>
<tr>
<td>silica shell thickness of ~12 nm</td>
<td>~81</td>
<td>122±3</td>
<td>18±2</td>
<td>119±2</td>
</tr>
</tbody>
</table>

It is worth emphasising that the synthesised doped Ag/SiO$_2$ nanocomposites were bright enough to be observed individually, especially after MEF. In order to confirm this, we compared images of nanocomposites taken by the time-gated fluorescence microscope and SEM (Fig. 6). They clearly demonstrate that each measured dot in the microscope image was, indeed, a single nanocomposite. The average value of the peak intensity in the fluorescent core/shell nanocomposites observed in these images was approximately ~8.9-fold higher than that of the corresponding silica nanoshells, while in the ensemble measurement a similar factor of 9.5 was obtained.
4. CONCLUSIONS

In this work, the fluorescence enhancement and lifetime decrease of the Eu chelate, BHHCT-Eu-DPBT, in Ag/SiO$_2$ nanocomposites were observed. The changes in fluorescence enhancement and lifetime were also investigated by tuning the thickness of the silica shell and diameter of the Ag core. A significant fluorescence enhancement and lifetime decrease of BHHCT-Eu-DPBT were acquired in such nanocomposites having the silica shell of ~12 nm and Ag core of ~52 nm. The origin of the observed enhancement is attributed to an increase of the intrinsic decay rate of fluorophores close to metal nanostructures. This promising core-shell nanocomposite will have great potential in time-gated bioassay and bioimaging with strong emission signals but low emission background. This can be attributed to the following reasons. Firstly, they have a total diameter of ~100 nm, enabling them immuno-interaction with the targets on the cell surfaces or even permeate through the cell membrane and conjugate with the targets in the cells. Secondly, the lifetimes of doped Eu chelates in such core-shell nanocomposites still remain to be much longer than the cellular autofluorescence.

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