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Fluorescence Enhancement by Metal-Core/Silica-Shell Nanoparticles**

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The fundamental and applied physics of noble-metal nanoparticles is currently attracting much attention. To a great extent this is due to promising new applications of noble-metal colloidal nanoparticles in fields such as materials science,[1] biophysics,[2] molecular electronics, and fluorescence-spectral engineering based on surface-enhancement effects.[3] In particular the nanoparticles have promising applications as bright fluorescent markers with enhanced photostability in fluorescence microscopy, sensor technology, and microarrays. The enhancement of the fluorescence emission of molecules near a metal surface arises from interactions with surface plasmon (SP) resonances in the metal particles.[4–6] These interactions may also result in shortening of the excited-state lifetime thus improving the photostability of the dye.[7]

The optical properties of a fluorescent molecule located near a metal nanoparticle are affected by the near-field electrodynamical environment.[4–6] This can cause an enhancement or quenching of the fluorescence depending on the distance between the molecule and the metal surface. In the case of fluorescent molecules located at very short distances from a metal surface, non-radiative energy transfer to SPs in the metal takes place.[8,9] Electromagnetic-field enhancement due to SPs, however, still occurs at longer distances from the metal core. As a result, there is an optimal fluorescent molecule to metal-core distance for fluorescence enhancement.

Important factors affecting the strength of the fluorescence enhancement are the size and shape of the nanoparticle, the orientation of the dye dipole moments relative to the nanoparticle surface normal, the overlap of the absorption and emission bands of the dye with the plasmon band of the metal, and the radiative decay rate and quantum yield (Q) of the fluorescent molecules.

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Fluorescence enhancement is usually expressed in terms of the apparent quantum yield Y_{app}, the ratio of the number of emitted photons in the presence of enhancement, and the number of absorbed photons in the absence of enhancement. For a molecule near a metal spheroid, which is small compared to the wavelength, a theoretical expression was derived for Y_{app} by Gersten and Nitzan.[4] Here, Y_{app} is written as a product of terms responsible for enhancement of the absorption rate (A^2), enhancement of the emission rate (E^2), and change of the decay rate of the fluorescent molecule relative to the non-interacting molecule $(\Gamma^{\mathrm{f}}/\Gamma)^2$.

$$Y_{\mathrm{app}} = A^2(\varepsilon_{\mathrm{core}},\omega_{\mathrm{ex}},\psi(a,b,d,\Theta,\Phi))\cdot E^2(\varepsilon_{\mathrm{core}},\omega_{\mathrm{fl}},\psi(a,b,d,\Theta,\Phi))\cdot(\Gamma^{\mathrm{f}}/\Gamma)^2 \qquad (1)$$

The distance dependence in Equation 1 is given by the factor $\psi(a,b,d,\Theta,\Phi)$. Here, a and b are the semimajor and semiminor axes of the core respectively, and d, Θ, and Φ are spherical coordinates of the dye molecule with respect to the core. In addition Y_{app} depends on the orientation of the transition-dipole moments of the dye molecule.

The SP-based enhancement of fluorescence by one- and two-photon excitation has been demonstrated experimentally.[7,10–13] However, most studies indicating fluorescence enhancement were carried out on molecules or films consisting of metal islands.[12,13] A few studies have been reported on colloid-based systems; most of these were carried out on planar sandwich structures consisting of a colloid-coated surface, a spacer layer, and a dye layer.[7,10,11]

More recently a number of studies were carried out on small particles consisting of a metal-core, spacer molecules, and fluorescent dye.[9,14–16] Fluorescence enhancement was not observed in any of these studies. The dye–metal distances in these studies were comparatively small (1–16 nm) and in some cases flexible spacer molecules were employed.

Here, we report on the observation of the enhancement of fluorescence by nanoparticles consisting of a metal core, a silica-spacer shell of variable thickness, and a dye-labeled shell. Gold and silver were chosen as core metals because their plasmon-resonance bands are located in the visible range of the spectrum (see Fig. 1) and match the absorption and emission bands of standard dyes. The spacer thickness was close to the theoretical optimal spacer thickness calculated using Equation 1, in combination with discrete dipole-approximation-based calculations.[17] The latter were included so as to take into account the different positions of the dye molecules with respect to the metal core and surface irregularities of the core.

For the dye molecules and metals employed here, the calculations yielded optimal spacer thickness in the range 20–30 nm. The spacer distances used here, resulted in average dye–metal distances of ~25, 24, and 15 nm for the Au-FAM (FAM: carboxyfluorescein), Ag-CYe (CYe: cascade yellow), and Au-CYe particles, respectively. The most important properties of the nanoparticles relevant to fluorescence experiments are summarized in Table 1.

FAM-Labeled Nanoparticles: The absorption and fluorescence efficiencies of FAM are pH dependent due to the presence of several prototropic forms of the molecule.[18] This allows tuning of the fluorophore Q by changing the pH. Low, 0.36, and high, 0.93, Q FAM states were obtained using solutions of pH 2.4 (5 mM KH_2PO_4 buffer) and 9.5, respectively.[18] Distributions of different prototropic states of FAM molecules occur, biased towards the low and high Q states of the dye. Moreover, the low Q prototropic form of FAM has its absorption maximum at 440 nm with the high Q form exhibiting a maximum at 490 nm. This allows further selection of the low and high Q state of the dye by exciting at 440 and 488 nm, respectively.

The permeability of the silica shell for H^+ and negatively charged ions was verified by recording excitation spectra of reference nanoparticles at high and low pH. The shapes of these spectra were in good agreement with the absorption spectra of FAM solutions[18] and changed virtually instantaneously following a change in pH.

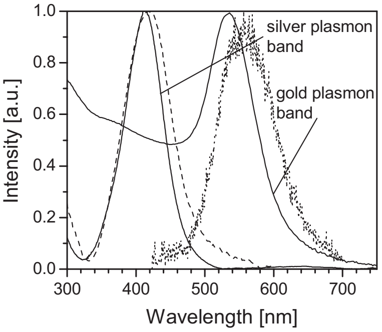

Figure 1. The absorption (dashed) and emission (dotted) spectrum of CYe and the plasmon bands of silver and gold.

Table 1. The structure and optical parameters of nanoparticles.

Core	Dye	Core diameter [nm]	Spacer thickness [nm]	Dye-shell thickness [nm]	Average dye–metal distance [nm]	Dye molecules per particle	Fluorescence lifetime [ns]	Enhancement factor
Gold	FAM	29.5	19.5	11.9	25	23	3.1	6.8/1.0[a]
	CYe	31.2	11.5	7.6	15	50	1.06	0.28
Silver	CYe	47.2	19.8	8.6	24	68	1.95	12.5
Reference	FAM	85.4	–	16.1		107	4.3	1
Reference	CYe	85.4	–	16.1		120	5.1	1

[a] At low pH no enhancement was observed; at high pH the enhancement amounted to 6.8.

The fluorescence intensity of FAM incorporated in the gold-core/silica-shell nanoparticles strongly depends on pH. At high pH and 490 nm excitation (high Q) the fluorescence intensity of the gold-core colloids showed no enhancement, Figure 2A.

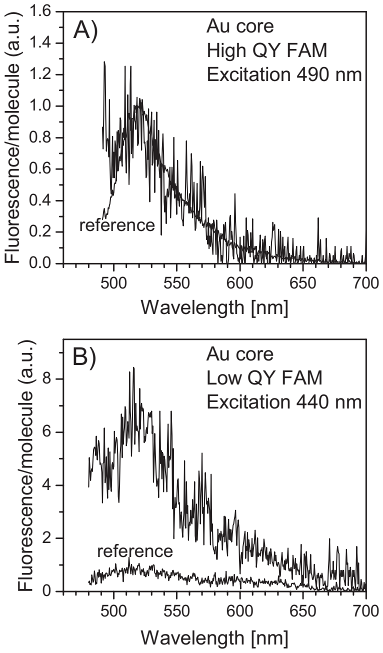

Figure 2. Emission spectra of FAM in gold-core and reference nanoparticles, excited at A) 490 nm, B) 440 nm.

In contrast, measurements at low pH and 440 nm excitation (low Q) exhibited a 6.8-times enhancement of the fluorescence intensity, Figure 2B. In both cases the excitation wavelength is well outside the maximum of the gold plasmon band (see Fig. 1). Therefore, absorption enhancement, due to the interaction of the exciting electromagnetic field with the SPs, is expected to be small. In contrast, the emission band of the dye does overlap the gold plasmon band, so that emission may be enhanced.

The average fluorescence lifetime of FAM in the reference specimen was found to be 4.3 and 3.6 ns at high (490 nm excitation) and low (440 nm excitation) pH, respectively. Furthermore, the width of the lifetime distribution at low pH was broader than that at high pH. This is caused by the presence of a distribution of different prototropic states of the dye at low pH. In the presence of a gold core, the fluorescence lifetime of FAM decreases to 3.1 ns. Surprisingly, in this case the pH does not appear to affect the fluorescence lifetime. Shortening of the lifetime, with respect to the reference particle, is in agreement with the enhancement of the emission rate. In the case of low Q FAM, the enhancement of the emission rate will result in an increase in the quantum yield of the dye ($Q = \mathrm{K}_{\mathrm{rad}}/\mathrm{K}_{\mathrm{rad}} + \mathrm{K}_{\mathrm{non\text{-}rad}}$) and a lowering of the fluorescence lifetime ($\tau = 1/\mathrm{K}_{\mathrm{rad}} + \mathrm{K}_{\mathrm{non\text{-}rad}}$).

CYe-Labeled Nanoparticles: In addition to the FAM-labeled nanoparticles, CYe-labeled particles with silver and gold cores were investigated. CYe has a quantum efficiency of about 0.56,[19] the absorption maximum is at 405 nm and the broad fluorescence band peak is at 550 nm, see Figure 1. While the absorption band of CYe does not significantly overlap the plasmon band of gold, a significant overlap of the emission band is observed. Consequently, only emission enhancement is expected in this case. In contrast, the absorption band of CYe overlaps the plasmon band of silver, though the emission band exhibits only a limited overlap with the silver-plasmon band. In this case, an absorption enhancement is possible for CYe-labeled, silver-core nanoparticles.

Normalized fluorescence-emission spectra of solutions of CYe-labeled, metal-core nanoparticles and of CYe-labeled, silica (reference) particles are shown in Figure 3A. All spectra were recorded at 405 nm excitation. The silver-core nanoparticles showed a strong, 12.5-fold fluorescence enhancement. The fluorescence of CYe-labeled gold-core nanoparticles was quenched. The intensity decreased by a factor of four.

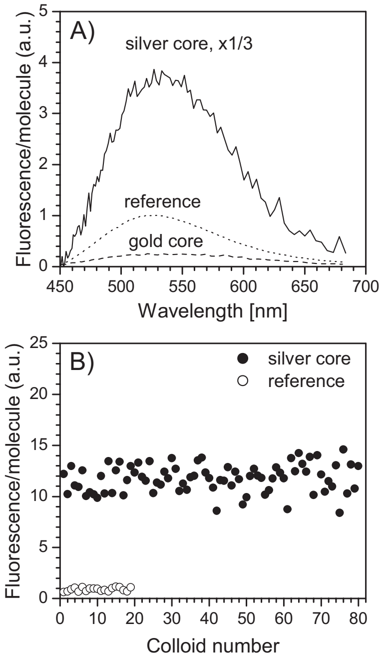

Figure 3. A) Average fluorescence emission spectra per dye molecule (silver-core particle emission, scale 3x reduced), B) single-particle fluorescence intensity per dye molecule.

The CYe-labeled, silver-core particles were also investigated at the single-particle level using a confocal microscope. To this end nanoparticles were adsorbed on a glass cover slide and the fluorescence intensities of single particles were measured. In these experiments we occasionally noticed fluorescence spots with twice and three times the average spot intensity. These spots were due to the presence of two or three nanoparticles in the detection volume of the confocal microscope. Such spots were excluded from the analyses. The intensities of 80 single CYe-labeled, silver-core nanoparticles and 20 single, CYe-labeled reference particles were measured. The fluorescence intensities of both the silver-core and the reference particles were normalized by dividing the measured intensities by the average number of dye molecules per particle. The results of the experiments are summarized in Figure 3B.

The average normalized metal-core nanoparticle intensity is about 12.5 times larger than that of the reference particles. Variation in the intensity is somewhat larger than expected from the number of dye molecules in the particles. This is likely to be caused by variations in the orientation of the dye molecules in the particles. The intensity variations are too small to be accounted for by aggregation of particles.

Single CYe-labeled, gold-core nanoparticles were very hard to detect in the confocal microscope due to their low-fluorescence signal. Therefore, no accurate single CYe-labeled gold-core nanoparticle measurements could be made.

Fluorescence-lifetime measurements on the reference nanoparticles showed a mono-exponential decay with a lifetime of 5.1 ns. Both silver-core and gold-core nanoparticles exhibited multi-exponential fluorescence decays. The nanoparticles are indeed expected to exhibit a distribution of decay times. The decay time of individual dye molecules depends on the orientation of the dipole moment of the dye molecule relative to the metal-core surface, as well as the dye–metal distance. Dye orientation and dye–metal distance distributions are present in the nanoparticles. In addition, the metal cores of nanoparticles exhibit polydispersity in size and morphology.

The decays of CYe-labeled, metal-core/silica-shell nanoparticles were significantly shorter than those of reference particles without a metal core. In the case of the silver-core nanoparticles the mean CYe fluorescence decay time went down from 5.1 to 1.95 ns. Reduction of the fluorescence-decay time of CYe in gold-core nanoparticles was stronger; the mean decay time went down to 1.06 ns.

The quenching of the fluorescence intensity and the pronounced shortening of the lifetime of the CYe-labeled, gold-core particles indicates that, in this case, non-radiative energy transfer to surface plasmons takes place.

These findings clearly show that the nanoparticles can exhibit fluorescence enhancement when sufficiently large distances between the dye molecules and the metal surface exists. Previous studies on particles consisting of a metal core, (flexible) spacer molecules, and fluorescent dye[9,14–16] showed no fluorescence enhancement. All of these studies showed fluorescence quenching and a reduction of the fluorescence lifetime. However, the dye–metal distances in these studies were comparatively small (1–16.2 nm) and the use of flexible spacer molecules may have reduced the effective distance. Interestingly, one of the above studies showed a clear reduction of the quenching effect at longer distances.[16] Here, the maximum distance amounted to ~16.2 nm. In our work quenching was observed at an average metal–dye distance of 15 nm and clear enhancement at 24–25 nm.

Additionally, during the imaging experiments on the CYe-labeled nanoparticles, we observed increased photostability of the metal-core particles relative to the reference particles. This is expected, as photodegradation is usually associated with excited-state reactions and therefore a reduction of the lifetime will result in increased photostability. The photostability of dye-labeled, metal-core nanoparticles will be investigated in more detail in future experiments.

The dye-labeled, metal-core/silica-shell nanoparticles are an excellent model system to study interactions between fluorescent molecules and metals. The use of a silica spacer layer allows easy tuning of the dye–metal distance to large enough values for enhancement to occur. The shape and size of the metal core can be changed to further control the optical properties of the particles. Finally, the particles are potentially interesting as bright fluorescent labels in, for instance (single-particle) imaging experiments or bioassays.

Experimental

Gold colloids with a diameter of 30 nm were synthesized according to the standard sodium citrate reduction method [20]. Silver colloids with a diameter of 46 nm were purchased from Ted Pella Inc. Two silica shells were grown around the particles using a method described elsewhere [21]. The first shell served as a spacer between the dye molecules and the metal core and the second shell contained both silica and dye molecules. The silica outer shell of the gold-core nanoparticles was labeled with FAM succinimidyl ester or CYe succinimidyl ester and the silver-core nanoparticles were labeled with CYe according to the procedure given in [22]. Colloids without a metal core served as a reference. The absence of aggregates in the solutions was confirmed by carrying out absorption spectroscopy at every stage of the particle synthesis. The absorption spectra did not exhibit additional bands shifted to long wavelengths, as expected when aggregation occurs. Moreover, no aggregates were visible in transmission electron microscopy (TEM) images (not shown) for specimens prepared in a similar way as the specimens used in the confocal imaging experiments

TEM on the particles was carried out using a Philips CM10 microscope. A TEM image of gold-core/silica-shell nanoparticles is shown in Figure 4. In this figure some aggregation is visible due to the comparatively high particle concentration in combination with drying effects.

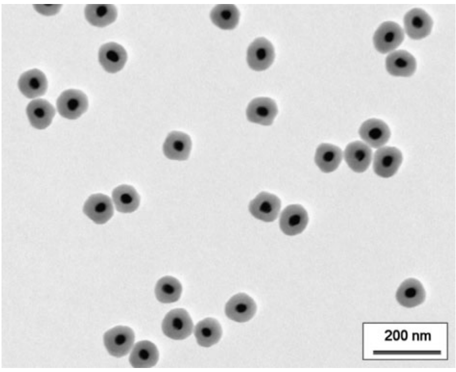

Figure 4. TEM image of FAM-labelled gold-core (30 nm) silica-shell nanoparticles.

The diameter and polydispersity of the particles were determined using image-processing software. The average structure parameters ($N=300$) of the metal-core/silica-shell colloids used in the experiments are summarized in Table 1.

At the dye concentrations employed here, the average distance between the dye molecules was at least 12 nm. This assures that no interactions between dye molecules occurred [22]. The mean number of dye molecules per particle was determined by dissolving the particles in a high pH solution (0.4 M NaOH mixed with ethanol 1:1) [23]. Next, the fluorescence intensity of the solution was measured and compared with a reference specimen of known concentration.

Average fluorescence lifetimes were recorded using a confocal microscope (Nikon PCM 2000) equipped with a four-channel time-gated detection system (LIMO) [24]. Full fluorescence decay curves were recorded using the same microscope in combination with a time-correlated single-photon-counting (TCSPC) board [25]. Lifetimes were extracted by fitting to a (multi)exponential function taking into account the system response.

The solution measurements were carried out on a Perkin Elmer LS50B spectrometer at particle concentrations of 10^{13} and 5×10^{13} particles/L for the metal-core and reference particles, respectively. This is sufficiently low to avoid unwanted interactions between the particles. Moreover, at these particle concentrations the absorption of fluorescence and excitation light by surface plasmons is very small (<2 %). The excitation and emission responses of the instrument were corrected for and all data were corrected for scattering and other background signals. We note that emission due to the metal core and the silica amounted to a few per cent of the total signal intensity of the labeled particles and was determined by carrying out control measurements on non-labeled metal-core/silica-shell colloids.

In the imaging experiments FAM and CYe were excited at 488 nm (CW Ar-ion laser), 440 and 405 nm (pulsed laser diode). The emission was selected using a 505 nm dichroic mirror and emission filters (500 nm long-pass filter or a 535/40 nm band-pass filter).

The fluorescence intensities of single nanoparticles (metal core and reference) were normalized by dividing the measured intensities by the mean number of dye molecules per particle. The fluorescence spectra of nanoparticles were normalized by division with the number of dye molecules per particle and the particle concentration (Figs. 2,3A). Next, the emission spectra of the reference and metal-core particles were scaled by the same factor, chosen such that the maximum of the reference spectrum equalled 1.

The difference in noise level of the emission spectra is accounted for by the difference in particle concentration and number of dye molecules per particle. The concentration of dye molecules in the solution of FAM-Au particles was 23 times lower than that of the reference particles.

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Bending of a Carbon Nanotube in Vacuum Using a Focused Ion Beam[**]

By *Byong C. Park*,[*] *Ki Y. Jung*, *Won Y. Song*, *Beom-hoan O*, and *Sang J. Ahn*

Carbon nanotubes (CNTs) are graphitic tubules with nanometer-sized diameters and high aspect ratios.[1] They exhibit exceptional mechanical and electrical properties that are attractive for a variety of applications.[2,3] In many cases, however, the manipulation and modification of CNTs is required to realize their full potential. It is essential, for instance, to control the orientation and the length of CNTs in applications

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