

Enhanced Luminescence of CdSe Quantum Dots on Gold Colloids

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ABSTRACT

We have studied the enhancement of luminescence of (CdSe)ZnS core-shell quantum dots on gold colloids as a function of semiconductor nanocrystal-metal nanoparticle distance. Using a layer-by-layer polyelectrolyte deposition technique to insert well-defined spacer layers between gold colloids and quantum dots, a distance-dependent enhancement and quenching of quantum dot photoluminescence has been observed. The maximum enhancement by a factor of 5 is achieved for a 9-layer spacer (≈ 11 nm). The efficient quantum dot excitation within the locally enhanced electromagnetic field produced by the gold nanoparticles is evidenced by the observation of the surface plasmon resonance in the photoluminescence excitation spectrum of (CdSe)ZnS nanocrystals.

Spontaneous emission of light by molecules and atoms at nanostructured metallic surfaces is noticeably modified because of a complex interplay of enhancing and quenching physicochemical processes.^{1–5} Enhancement of photoluminescence (PL) can be promoted by surface plasmons excited in metal and by a modified density of photon states in a nanostructured surface.⁶ Quenching processes include chemical bonding and nonradiative energy transfer from the luminescent species to the metal. The modification of PL from atoms and molecules located near metallic nanostructured surfaces and nanobodies is an interesting subject in nanoscience, and its study gives new insights into the basic aspects of field-matter interaction.⁷ It is well established that molecules adsorbed at rough metal surfaces with metal islands, needles, or pyramids on the order of 100 nm show strong surface enhanced raman scattering (SERS). This phenomenon has been the subject of extensive research in the 1980s^{8,9} and is used as a basis for ultrasensitive analytical techniques in molecular science, biology, and medicine.^{10,11} Semiconductor nanocrystals (quantum dots, QDs) possess a number of advantageous features, such as light emitters^{12,13} and fluorescent labels,^{14,15} as compared to ionic and molecular chromophores. For example, a reduction of fluorescence

blinking behavior has been reported recently for (CdSe)-ZnS core-shell nanocrystals deposited on rough metal surfaces.¹⁶

In this letter we report on observation of an analogue to SERS—the pronounced enhancement of photoluminescence of semiconductor nanocrystals near nanostructured metal surfaces—which is shown to depend essentially on nanocrystal-metal spacing in the range of a few nanometers. The evidence of an efficient quantum dot excitation within the locally enhanced electromagnetic field produced by the gold nanoparticles we consider as a first step toward the goal to establish correlations or anticorrelations in spontaneous emission and Raman scattering of light by molecules and semiconductor nanocrystals (quantum dots) adsorbed on *periodic* metal-dielectric nanostructures.¹⁷

The first aim of this work is to use a supported gold colloidal film and polyelectrolyte multilayer spacer to examine the sensitivity of enhanced luminescence with respect to the distance between quantum dots and gold colloids. The spherical monodisperse colloidal gold nanoparticles exhibit a well-defined plasmon resonance around 550 nm, which can be used to excite resonantly the (CdSe)-ZnS nanocrystals. Unlike conventional SERS, the surface enhanced PL should exhibit nonmonotonic character with distance between the emitting dipole (QD) and nanostructured metal surface (Au colloid). The reason is that at smallest distances when QDs and colloids are in close contact, the QD emission should be damped due to resonant

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energy transfer (RET) from photoexcited QDs to metal colloidal nanoparticle.

An effective quenching of dye molecule PL by a single Au nanoparticle has been demonstrated earlier using a molecular beacon approach.¹⁸ Our basic assumption is that PL quenching is a short-range effect and it would be weakened with distance much faster than the enhanced electromagnetic field possibly responsible for the expected enhancement in PL. At a certain distance, which is assumed to be in the range of 5–10 nm, the enhanced QD emission would exhibit a maximum. Further increase in the dot–colloid distance results in a decrease of PL intensity to the level of that for QDs without any metal colloids (“quasi-infinite” distance). Thus, the key element of our approach is the controlled placement of spacer material between CdSe QDs and Au colloids with well-defined thickness. The polyelectrolyte multilayer coating¹⁹ is considered here as the best choice to achieve this goal. Layer-by-layer deposition from aqueous solutions of two types of oppositely charged polymers, usually positively charged polydiallyldimethylammonium chloride (PDADMAC, polycation) and negatively charged sodium polystyrene sulfonate (PSS, polyanion), produces a multilayer film via electrostatic interaction between oppositely charged macromolecules. The thickness of such film can be controlled precisely by a number of deposited layers from approximately 1.4 nm for the first layer to 33.9 for the 21st layer, for example.¹⁹ Finally, oppositely charged (relative to PDADMAC) QDs can be deposited on the surface of polyelectrolyte spacer in the form of a submonolayer film.

(CdSe)/ZnS core–shell QDs were synthesized via standard high-temperature reaction in TOPO/HDA mixture.²⁰ The diameter of QDs is about 8 nm, and the PL band is centered at 645 nm. QDs were solubilized in water according to known procedures¹⁵ using sodium mercaptoethylsulfonate (SMES) as solubilizing agent, which brings also a strong surface negative charge on QDs. Gold colloids of 12–15 nm in diameter were synthesized by citrate reduction of diluted HAuCl₄ aqueous solution.²¹ Gold nanoparticles are charged negatively due to chemisorption of citrate ions. A monolayer of gold nanoparticles was formed by electrostatic deposition onto glass slides covered with a layer of polycation. The absorption spectrum of gold colloidal film shows the well-known surface plasmon (SP) band (Figure 1 a). As has been shown in studies of the optical properties of gold nanoparticles embedded in glass or polymer (refs 22–24), the absorption band peaking around 540 nm is a typical signature for small isolated gold nanoparticles. We examined the morphology of our gold colloidal films on glass with atomic force microscopy and found that the gold nanoparticles form a monolayer with a small amount of aggregates (Figure 1b).

To cover the gold film with polyelectrolyte layers, we adopted the method described in ref 25. Briefly, a gold colloidal film on glass was dipped into PDADMAC solution, rinsed by water, then dipped into PSS solution and rinsed again. The operations were repeated to achieve a desirable number of polyelectrolyte layers. The last layer was always

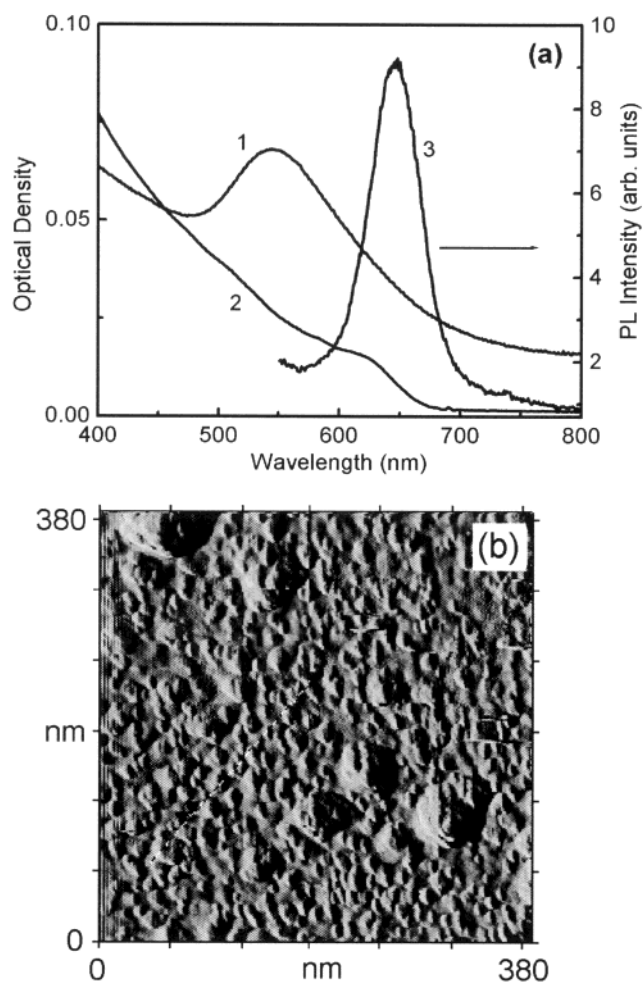


Figure 1. (a) Absorption spectra of Au colloidal film on glass (1), (CdSe)/ZnS QD film on glass (2), and PL spectrum of QD submonolayer on glass (3). $\lambda_{\text{PL excitation}} = 450 \text{ nm}$. Note that here a representative absorption spectrum of a thicker QD film is represented, because the absolute absorption of the QD submonolayer on gold/polyelectrolyte is much smaller and below the sensitivity of our experiment. (b) Differential AFM image of Au colloidal film on glass. The AFM image of the Au colloidal film surface was recorded in air using a Nanotechnology P4 AFM/STM microscope. The Si₃N₄ cantilever tip used had a spring constant of 0.4 N/m. The tip was pyramidal in shape and the tip radius was 10 nm.

PDADMAC. The sample was dried at room temperature, and a diluted aqueous solution of QDs stabilized with SMES was dropped and gently distributed over the whole sample surface. It is important to note that we dropped the same amount of QDs solution (0.05 mL) on each sample $1.5 \times 1.0 \text{ cm}^2$ in size. After drying, a set of samples was obtained in the form of gold colloidal films covered by a polyelectrolyte spacer of different thickness, but an equal amount of QDs on each sample. The experimental error in PL intensity is thus reduced down to 30% and determined mainly by the spatial inhomogeneity in the CdSe quantum dot coverage.

Room-temperature PL and PLE spectra of samples were recorded by a Jobin-Yvon Fluoromax-2 spectrometer. First, PL spectra of samples with different thickness of polyelectrolyte spacer were measured with the excitation wavelength, corresponding to the maximum of plasmon resonance in the

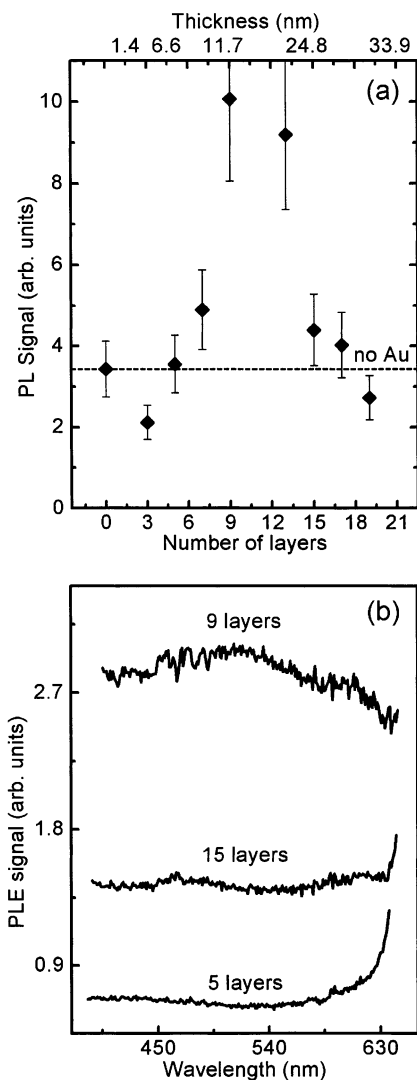


Figure 2. (a) QD-PL intensity versus number of polyelectrolyte layers between QDs and gold colloids. The upper x -axis indicates the approximate thickness in nm of the corresponding polyelectrolyte spacer (data adopted from ref 19). The horizontal dashed line shows the PL intensity of the same amount of QDs deposited on glass without gold colloids (reference sample). $\lambda_{\text{excitation}} = 550$ nm. (b) Differential PLE spectra of three samples with 5, 9, and 15 polyelectrolyte spacer layers between QDs and gold colloids. All three spectra were divided by a reference PLE spectrum taken for QDs on glass without gold colloids. $\lambda_{\text{emission}} = 650$ nm.

absorption spectrum of the gold colloidal film ($\lambda = 550$ nm). The enhancement of PL is expected to be most pronounced when excited at the frequency of surface plasmon resonance in gold colloids. Figure 2a shows the magnitude of the QD PL band for different thickness of polyelectrolyte spacer up to about 30 nm (19 layers).¹⁹ The upper x -axis in Figure 2a is given in nanometers using the layer calibration of ref 19 (note that with increasing spacer thickness the individual layer thickness slightly decreases so that the total thickness is not a linear function of the first layer). The polyelectrolyte spacer itself should not influence the PL signal from QDs. Both PDADMAC and PSS do not absorb in the visible region and do not quench the QDs emission. The important result of Figure 2a is that the PL intensity is sensitive to the distance between gold colloids and QDs and exhibits a maximum at

around 9 layers (≈ 11 nm) of the polyelectrolyte film. In the absence of polyelectrolyte layers (zero point in Figure 2a but not yet zero distance between QDs and gold colloids, since QDs carry approximately 1 nm in length the surface monolayer of SMES molecules), the PL signal is dropped by a factor of 3 relative to the maximum. This observation is in agreement with recent reports about a quenching of PL due to resonant energy transfer (RET) observed for molecular systems at metallic surfaces.^{26,27} Surprisingly, the 19-layer polyelectrolyte spacer (largest achieved in our experiment) gives rise to a PL signal which is comparable to that for zero layers within the experimental error. We may conclude that RET, which is mainly responsible to a quenching of QD emission, is very efficient at very short distances between QDs and gold colloids and can completely compensate the effect of enhanced PL. Hence, in the hypothetical case of absence of RET, we expect in such systems an even larger effect of PL enhancement. RET is not the only mechanism responsible for quenching of PL, especially for QDs in close contact with gold colloids. Electrons from photoexcited electron-hole pairs in QDs can tunnel and be captured in gold nanoparticles followed by nonradiative recombination with remaining holes at the QD-Au interface. The increase in potential barrier between QDs and gold colloids with the growing number of polyelectrolyte layers will drastically diminish the probability of photoelectron tunneling into gold. A comparison of enhanced PL effect on gold colloids and plain gold films could clarify this problem.

The mechanism of enhanced PL is not clear yet. Unlike SERS where both electromagnetic and chemical effects are important,⁸ enhanced PL is attributed mostly to the presence of a local enhanced electromagnetic field around metal nanostructures.²⁶⁻²⁸ Hence, the signature of the surface plasmon (SP) should be most pronounced in the PLE spectrum of the QD-Au structure with a 9-layer polyelectrolyte spacer and vanish for other spacer thicknesses. Figure 2b shows the PLE spectra of three samples with different number of polyelectrolyte layers. All experimental spectra were divided by the reference PLE spectrum of QDs on glass without gold colloids. The PLE signal of the 5- and 15-layer sample is spectrally constant showing no pronounced structures around the wavelength of the SP. The PLE spectrum of the 9-layer sample, however, consists of one broad green band centered at approximately 530 nm which correlates with the position of the SP band in the absorption spectrum of gold colloids (Figure 1a). The presence of SP-related replica in the PLE spectrum of the 9-layer sample supports our assumption that the excitation of the SP in gold colloids is responsible for the enhancement in the QD emission.

Summarizing, we propose that the locally enhanced electromagnetic field due to the plasmon resonance of colloidal gold nanoparticle results in a more effective QD excitation, as compared with the case of QDs in an electromagnetically inert environment (no gold colloids). Further experiment with other types of metal nanostructures, as well as plain metal films, will allow to clarify the details of QDs PL enhancement and quenching.

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