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Sensitized Fluorescence of Silver Nanoparticles in the Presence of Pyrene

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Abstract The fluorescence of pyrene adsorbed onto the surface of the cetyltrimethylammonium-coated silver nanoparticles was studied. Pyrene molecules adsorbed on freshly prepared silver particles were found to be in close proximity to silver surface thus providing the possibility of energy transfer from excited pyrene to silver cores of the particles. In that case along with the expected fluorescence of pyrene we observed the fluorescence of the silver nanoparticles induced by the excited pyrene molecules. In due course the restructuring of the cetyltrimethylammonium layer resulted in moving of pyrene molecules away from silver surface and simultaneous disappearance of the silver nanoparticles fluorescence band. These data strongly support the recent hypothesis of fluorophore-plasmon coupled emission.

Keywords Silver nanoparticles · Sensitized fluorescence · Pyrene

Abbreviations
CTMA   cetyltrimethylammonium
NPs   nanoparticles
EDPs   electron diffraction patterns

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Introduction

Metallic particles, surfaces, and nanostructures exhibit various optical properties. They include the intense color of metal colloids due to surface plasmon resonance absorption/scattering and modifying quantum yields of fluorophores in close proximity to metallic surface. Near surfaces of noble metals the fluorescence of excited fluorophores might either quench or enhance. In very rough outline the contemporary interpretation of the effect of metal surfaces on fluorescence is shifted to a model whereby nonradiative energy transfer occurs from excited distal fluorophores to the surface plasmon electrons thus decreasing the lifetime of fluorophore and increasing the quantum yield. The surface plasmons in turn, radiate. Some portion of the emitted radiation is further being absorbed by surrounding metal-containing medium. The ratio between the increasing of the quantum yield and the absorption determines whether the resulted far-field radiation is enhanced or quenched [1, 2].

Usually the radiation emitted by metallic structures is of the same wavelength as the emission wavelength of the fluorophore. In our experiments described in the present work we, however, observed that the fluorescent radiation emitted by silver nanoparticles in the presence of excited pyrene molecules does not correspond to the emission either of monomeric pyrene or known dimeric forms of pyrene including the excimers.

Experimental

Chemicals

Sodium borohydride (Lancaster, 98+%), Silver nitrate (99.9+%, Sigma-Aldrich), pyrene (Fluka, ≥99.0%, for fluorescence),

cetyltrimethylammonium (CTMA) bromide (Acros, 99+%), methylene chloride (Acos-1, for analysis) and n-hexane (Acos-1, for analysis) were used without further purification. All aqueous solutions were prepared with doubly distilled water.

Synthesis of silver nanoparticles

The preparation of cetyltrimethylammonium-capped silver nanoparticles (NPs) followed a modified two-phase protocol, which involved the preparation of a stable negatively charged silver bromide sol as Ag precursor, which can be transferred into the organic phase. First of all, an emulsion of water in methylenechloride was prepared by adding of 10 ml of water to a cetyltrimethylammonium bromide (0.44 g, 1.2 mmol, in 25 ml of CH_2Cl_2) solution. A silver bromide sol was preparing by dropwise adding of the 0.1 M $AgNO_3$ (1 mmol, in 10 ml of water) solution to the emulsion under vigorous stirring. After 15 min of stirring a sodium borohydride solution (0.08 g, 2 mmol, in 10 ml of water) was added dropwise to the obtained AgBr sol. During the addition of the reducing agent the color of the mixture became dark-red. The reaction was stirred for 1 h, and then organic phase was separated from water phase, yielding solution of the CTMA-capped silver NPs in methylenechloride.

Recording of absorption, emission, and excitation spectra

The absorption spectra of the sols were recorded in the visible range on a Specord M40 UV-VIS spectrometer (Carl Zeiss, Germany). The spectra were calibrated in the range 0.0–1.0; the mark 0.0 corresponded to the absorption intensity at 700 nm and the mark 1.0 corresponded to the intensity at the absorption band maximum.

The emission, and excitation spectra were recorded using a Jobin Yvon 3CS (Jobin Yvon, France) spectrofluorometer with a xenon gas-discharge lamp as a source of radiation. Working solutions were prepared immediately before the fluorescence measurements by addition of aliquots of silver NPs solution in methylenechloride to 3 ml of n-hexanic pyrene solution.

Recording and processing of micrographs

The micrographs of the samples were recorded on a Leo 912 AB Omega transmission electron microscope (Leo Ltd., Germany) at accelerating voltage of 100 kV. The samples were prepared by the deposition of a sol (1 μl to 2 μl) onto a copper grid coated with Formvar™ followed by drying in air. The size distribution of silver nanoparticles was calculated on the basis of obtained micrographs using the Femtoscan Online™ v.2.2.91 software package (Advanced Technologies Center, Russia).

Results and discussion

Silver NPs properties

The dark-red color of obtained organosol corresponds to the excitation of surface plasmons [3, 4]. In the UV-Vis extinction spectrum of the silver sol (shown in Fig. 1) an intense absorption band at 418 nm is present. Such position of the surface plasmon resonance band is typical for noncovalently stabilized silver NPs [5]. In our case the silver NPs are stabilized by cetyltrimethylammonium bromide.

It is well-known that silver nanoparticles are able to fluoresce under the intense excitation [6, 7]. The corresponding quantum yields significantly depend on the structure and size of particles. In order to estimate the intrinsic fluorescence of the synthesized NPs we recorded the emission spectra of the silver sol mixed with n-hexane (45 μl of the sol in 3 ml of n-hexane). While the silver NPs solution was excited at different wavelengths (337 nm, 385 nm, 440 nm, and 470 nm) the emission was below the detection limit. So, we could neglect the intrinsic fluorescence of the silver NPs during the further studies.

According to transmission electron micrographs of the freshly prepared colloid (Fig. 2a) the synthesized silver NPs are well-formed spheres of 1–15 nm in diameter. Most of the particles are of 4 nm in size (Fig. 2b). The electron diffraction patterns (EDPs) are noticeably diffuse thus indicating the presence of some defects in the crystal structure of the particles (Fig. 2c) but the type of the defects cannot be determined solely from the EDPs. Micrographs and diffraction patterns obtained in 2 days and 14 days after the synthesis show that two main processes occured: the growth and the crystallization of the NPs. The mean size of the NPs increased in 1.5 times in 14 days and the fraction
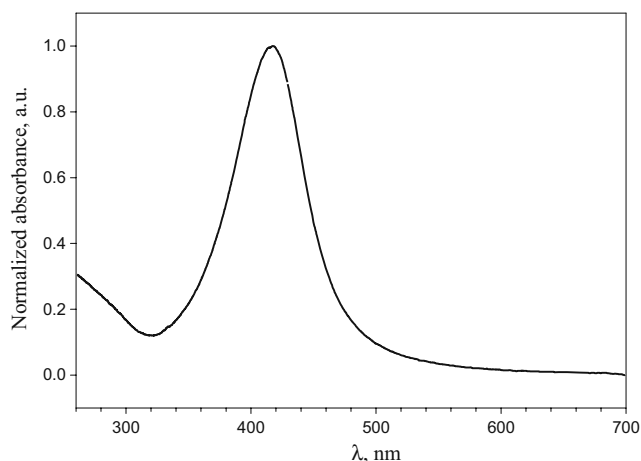
Fig. 1 The UV-Vis extinction spectrum of the cetyltrimethylammonium-capped silver NPs n-hexanic solution

Fig. 2 TEM micrographs **a** corresponding size distribution histograms **b** and electron diffraction patterns **c** of cetyltrimethylammonium-capped silver NPs immediately after the synthesis
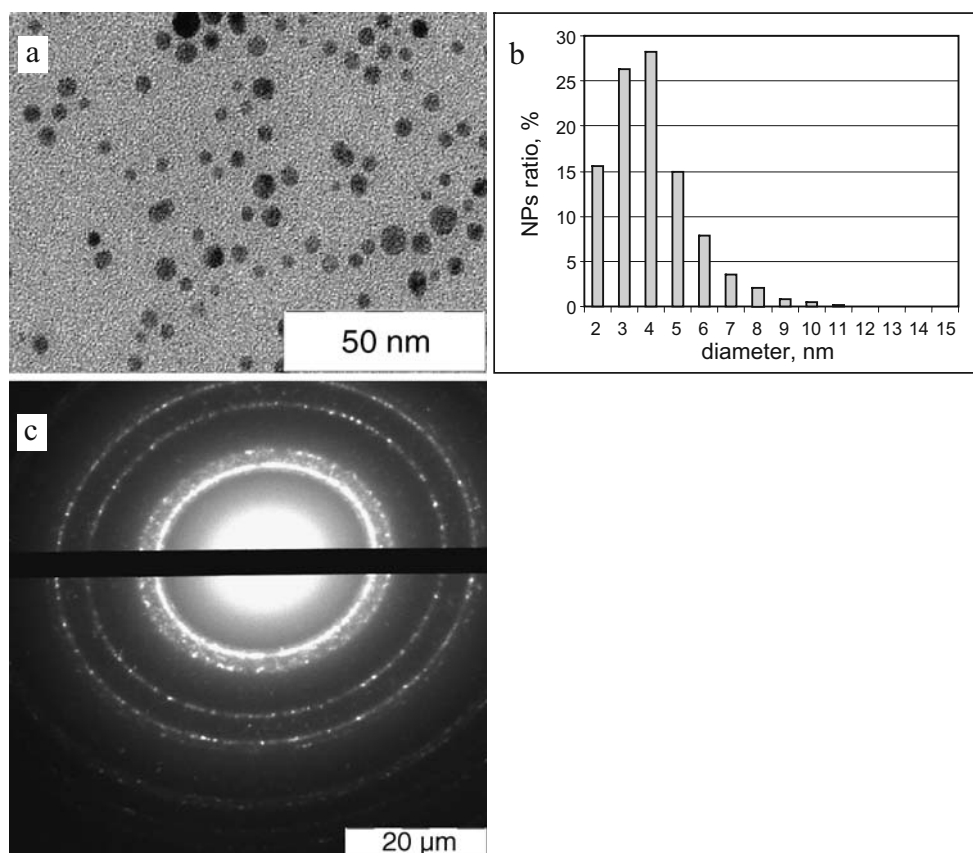
of the particles of 2 nm to 3 nm in size decreases from 42% to 17%. The EDPs became less diffused. The extinction spectra of the colloid didn't show any remarkable change.
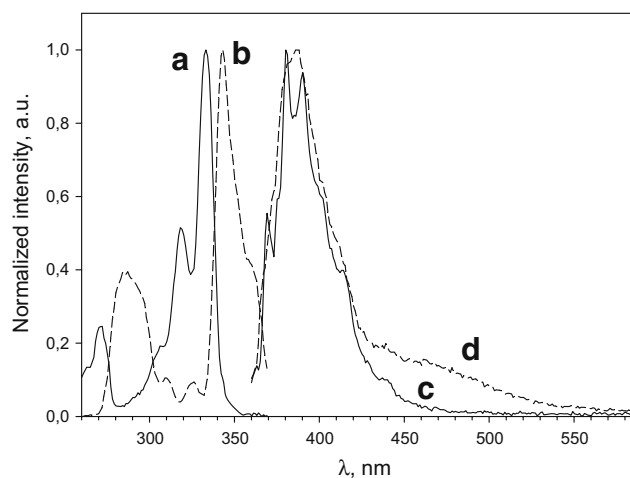
Fluorescence of pyrene solutions

We used two different pyrene solution in n-hexane: a concentrated solution ($5*10^{-4}$ M) and a diluted one ($5*10^{-6}$ M). The fluorescence excitation (collected at 380 nm) and emission spectra (excited at 337 nm) of both solutions are shown in Fig. 3.
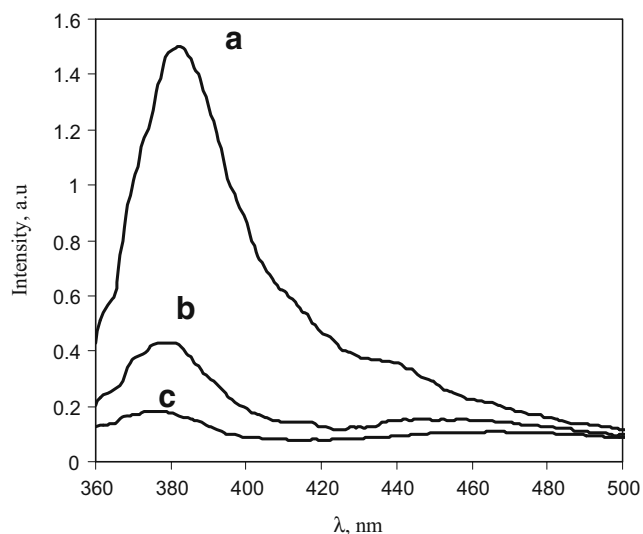
The emission spectra of the diluted solution have an intense band at 385 nm, and three bands at 270, 318 и 335 nm are observed in the excitation spectrum (Fig. 3a,c). Both spectra coincide with the corresponding spectra of the pyrene monomers (emission band at 380–400 nm [8], excitation bands at 240 nm, 275 nm, 325 nm, 340 nm [9]).

The excitation spectrum of the concentrated solution (Fig. 3b) strongly differs from the excitation spectrum of monomers and coincides with the excitation spectrum of pyrene dimers (5–10 nm red-shifted as compared to excitation spectrum of monomers [8, 10]). In the emission spectra of the concentrated solution along with an intense band at 370–420 nm with the maximum at about 390 nm (Fig. 3d) corresponding to emission of excited monomers of pyrene, a weak fluorescence at 430–480 nm, was

observed. This weak fluorescence could be associated with emission of pyrene excimers [8, 9]. Thus, having taken into account the fluorescence spectra we can conclude that in the diluted solution pyrene the main form of pyrene is monomeric while in the concentrated solution most of pyrene molecules form dimers.


Fig. 3 Normalized fluorescence excitation spectra of $5*10^{-6}$ M (**a**) and $5*10^{-4}$ M (**b**) n-hexanic pyrene solutions collected at 380 nm and corresponding emission spectra excited at 337 nm (**c**, **d**)

Fig. 4 Emission spectra of the diluted ($5*10^{-6}$ M) n-hexanic pyrene solution excited at 337 nm in the presence of 15 μl (**a**), 30 μl (**b**), and 45 μl (**c**) of silver NPs solution

Fluorescence of the diluted pyrene solution in the presence of silver NPs

The addition of 15 μl of silver NPs solution into the diluted pyrene solution($5*10^{-6}$ M) resulted in the blue-shift of the maximum of the emission band and in significant decrease of the emission intensity at 370–420 nm. Simultaneously the fluorescence of pyrene excimers appeared at 440 nm and 470 nm (Fig. 4). In the excitation spectra collected at 440 nm and 470 nm only the bands at 320 nm and 335 nm corresponding to the excitation of pyrene monomers were observed (Fig. 5). The coincidence of excitation spectra at these wavelengths confirms that the bands at 440 nm and 470 nm are due to pyrene excimers emission.
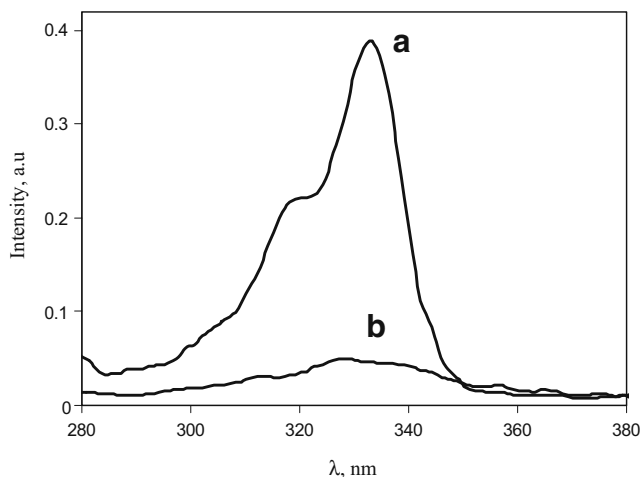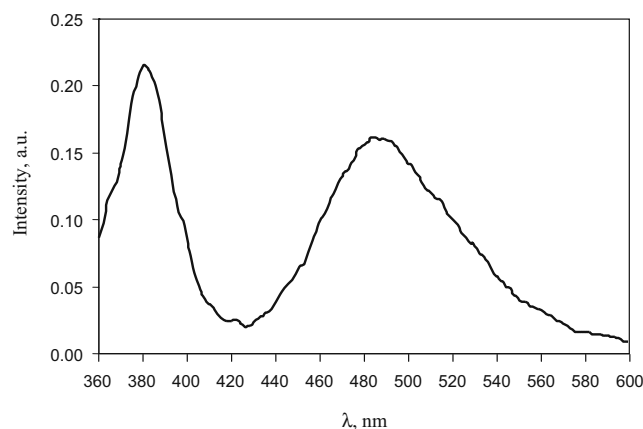
As we mentioned above the formation of excimers could be observed only if the concentration of pyrene solution is high enough. For example, the excimers' fluorescence did not appear in the fluorescence spectra of the diluted pyrene solution ($5*10^{-6}$ M). Hence, the excimers formation in the presence of silver NPs could be, probably, rationalized by the adsorption of pyrene on silver surface. This results in significant increase of pyrene concentration in the adsorption layer so that it forces excimers formation.

The intensity of the emission at 370–420 nm decreases upon the further addition of the silver NPs to the pyrene solution and the band position continues to blue-shift. The excimers' emission also decreases but considerably less. As a result, the excimers' fluorescence became more intense than the monomers' fluorescence upon the addition of 45 μl of silver NPs solution. The decrease of emission intensity in the presence of colloid silver could be explained by absorption and scattering of the emitted radiation by silver particles because their extinction spectrum match the same spectral region. Absorbance of the silver NPs solution at 470 nm is about 2.5-fold less than at 380 nm (Fig. 1), therefore the monomers' fluorescence decreased more significantly. Besides, absorbance of the CTMA-coated silver NPs in n-hexane at the long-wave boundary of the monomers' fluorescence band (390 nm) is about 1,7-fold greater than at the short-wave boundary (370 nm): ≈0.7 at 390 nm versus ≈0.4 at 370 nm (Fig. 1). This results in the remarkable distortion of the shape of the pyrene monomers' fluorescence band and in the seeming blue-shift of the emission maximum.

Fluorescence of the concentrated pyrene solution in the presence of silver NPs

The fluorescence spectrum of the concentrated pyrene solution ($5*10^{-4}$ M) containing silver NPs strongly depends

Fig. 5 Excitation spectra of the diluted ($5*10^{-6}$ M) n-hexanic pyrene solution collected at 440 nm (**a**) and 470 nm (**b**)

Fig. 6 Emission spectra of the concentrated ($5*10^{-4}$ M) n-hexanic pyrene solution excited at 337 nm in the presence of 45 μl of freshly prepared silver NPs solution.
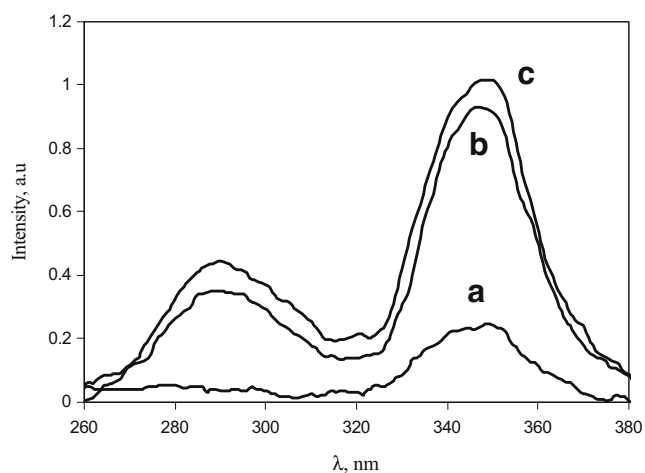
Fig. 7 Excitation spectra of the concentrated ($5*10^{-6}$ M) n-hexanic pyrene solution collected at 440 nm (**a**), 470 nm (**b**), and 490 nm (**c**)

on time elapsed since the moment of the silver NPs synthesis.

Upon the addition of 15 µl of freshly prepared silver colloid to the concentrated pyrene solution the emission of pyrene monomers at 380 nm remained, and a new intense emission band at 490 nm appeared in the fluorescence spectra (shown in Fig. 6). The intensity of this band decreased with time, and the fluorescence bands of pyrene excimers appeared simultaneously at 440 nm and 470 nm. The band at 490 nm disappeared completely in 10 h after the silver NPs synthesis.

The excitation spectra collected at 440 nm, 470 nm and 490 nm were not time-dependent and contained only broad

bands at 280–300 nm and 340–360 nm corresponding to pyrene dimers (Fig. 7).

The band at 490 nm does not correspond to any of the known forms of pyrene. Recently the authors [11] have shown that the emission spectra of pyrene adsorbed on silver surface contained only the typical bands at 380–400 nm (monomer emission) and at 470 nm (excimer emission). At the same time the band at 490 nm was absent.

Since the fluorescence excitation spectrum of the concentrated pyrene solution containing silver NPs coincides with the excitation spectrum of pyrene dimers, and the band at 490 nm does not correspond to any of the known forms of pyrene, it should be concluded that the emission at 490 nm is due to fluorophore-coupled radiating plasmons. This phenomenon involves excitation of the pyrene dimer and rapid energy transfer to the plasmons, which then radiate. An effective energy transfer might occur only if an excited fluorophore is in close proximity to silver nanoparticle, for example, if pyrene is adsorbed on nanoparticle surface.

We have already mentioned that the addition of the CTMA-stabilized silver nanoparticles to pyrene solutions forces adsorption of pyrene on silver NPs surface and formation of pyrene dimers. As reported in [12] the polar head of the adsorbed CTMA is located near silver surface while the nonpolar tail contacts with the solvent. Adsorbed pyrene can be located both in the polar and in the nonpolar layers. It is also known that in case of noncovalent surface stabilizers the complete formation of the adsorbed layer might finish in some hours after the synthesis of nanoparticles. Thus, the observed changes in fluorescence
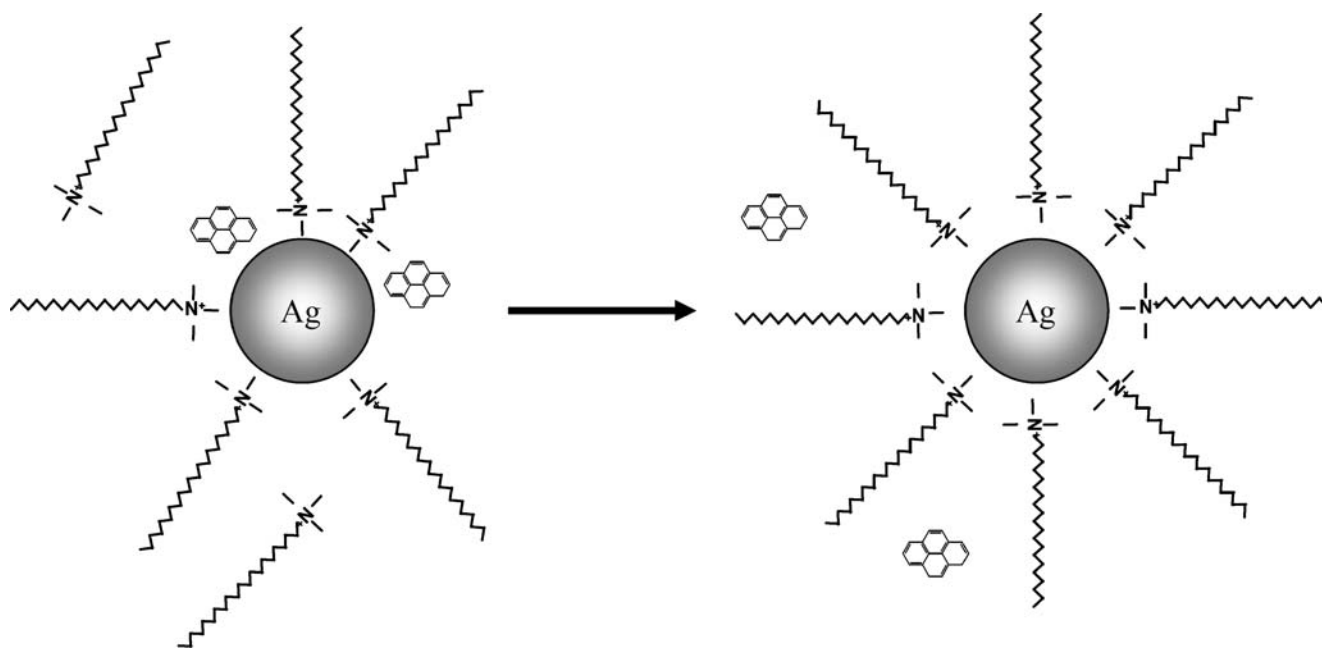
Fig. 8 Scheme of the rearrangement of pyrene and CTMA in the adsorbed layer

spectra are most likely connected with formation or restructuring of a stabilizer's layer. Immediately after the synthesis stabilizer molecules are not densely packed so that pyrene can adsorb directly on the particle surface or near it thus providing the possibility of the energy transfer to the silver nanoparticle. Then CTMA molecules start to displace pyrene on the silver surface and form a compact structure where pyrene is more distant from the silver surface and is probably located in nonpolar layer of CTMA. As it was demonstrated during our experiments this process completely finishes in approximately 10 h after the synthesis. This process is briefly schematized in Fig. 8.

The other possible time-dependent process which can influence on the fluorescence spectra is the aggregation of nanoparticles. We have mentioned above that this process actually occurred. But we did not observe a significant change in size distribution of nanoparticles even in 14 days after the synthesis. Besides, the increasing of the plasmon-coupled emission intensity with the increasing of the average particle size would be expected due to the increasing of scattering cross-section of silver nanoparticles [1, 2]. On the contrary the intensity of the band at 490 nm decreases with time. Thus, the changes in spectra can not be explained by the aggregation, so that the restructuring of the adsorption layer remains the most suitable explanation of the disappearance of band at 490 nm.

We additionally measured the lifetime at 470 nm of pyrene and pyrene in the presence of silver nanoparticles. It was found that the pyrene lifetime decreases upon addition of freshly prepared silver colloid from 140 ns to 70 ns. This confirms our suggestions about rapid energy transfer from pyrene to a silver nanoparticle because it is well-known that the lifetime of surface plasmons is very short, on the order of tens of femtoseconds [13, 14]. We weren't able to measure the correct quantum yield of pyrene due to the complexity of determination of exact contribution of each pyrene form (adsorbed and dissolved monomers and dimers) to the observed fluorescence.

In case of the diluted solution the concentration of pyrene is too low and the fluorescence band at 490 nm probably is not intense enough to be observed against the broad and intense excimers' emission at 440–500 nm.

Conclusions

In this paper we have shown that CTMA-coated silver nanoparticles can effectively adsorb pyrene from n-hexanic solutions, thus enabling the possibility of their use as new sorbents for preconcentration and following determination of pyrene and other polyaromatic hydrocarbons. The adsorption of pyrene was found to force the formation of pyrene dimers. We have also found that the restructuring of the CTMA layer adsorbed on silver nanoparticles' surface influence on the distribution of pyrene molecules in the adsorption layer. We have observed the fluorescence of the silver nanoparticle induced by the excited pyrene molecules. The appropriate explanation of this phenomenon is the energy transfer from the excited fluorophore to surface plasmons, which then radiate. The data obtained strongly support the recent hypothesis of fluorophore-plasmon coupled emission [1, 2].

Further studies of the fluorescence of pyrene adsorbed on silver nanoparticles by our laboratories are currently underway.

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