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Fluorescent silver oligomeric clusters and colloidal particles

Mona Treguer, Frederic Rocco, Gerald Lelong, Anne Le Nestour, Thierry Cardinal, Abdelhamid Maali and Brahim Lounis

Abstract :

Highly luminescent single colloidal silver nanoparticles under blue excitation were detected. The intense luminescence observed from the single particles is attributed to different emissive centers. Picosecond lifetimes of those single nano-objects have been measured. Comparison with colloidal particles emission formed in aqueous solution, using polyacrylate polyanion as stabilizer is drawn. The optical properties of silver colloidal particles in solution are observed while their surface is changed by deposition of silver ion. A large visible emission under UV or surface plasmon region excitations is observed for $Ag_n@Ag^+$, while no fluorescence emission was found for Ag_n or Ag^+ systems. The intense visible light emission changes should primarily come from chemical surface active sites. It was observed that the oligomeric clusters, composed of only few atoms Ag_{4+x}^{x+} and Ag_7^{3+} , have a substantial emission in the same visible region. A model which ascribes the photoemission of the chemically modified silver colloidal particle to oligomeric clusters on the Ag particle surface is proposed. Those emissive water soluble silver clusters have potential for biological labelling, and light emitting sources in nanoscale optoelectronics applications.

Keywords: Luminescence; Spectroscopy; Silver nanoparticles; Cluster; Optical microscopy; Photoactivation

1. Introduction

The physical properties of nanoparticles of noble metals have been widely studied for several years, in parallel to the efforts which have been devoted for the understanding of their elaboration and their nature. Besides their useful for biological labelling [1], [2] and [3] and their ability to promote surface enhanced optical phenomena [4], [5] and [6], it was discovered that noble metal clusters display intense visible luminescence. The appearance of their strong luminescence are expected to yield new insights into the practical applications in integrated optical devices (optical storage) or in biology (sensors). In the case of silver, it was shown that neutral clusters Ag_m ($m=2$ to 10) emit light in rare gas matrix at cryogenic temperature [7] and [8]. Dickson [9] and Tominaga et al. [10] have also observed the luminescence from silver oxide films or powders photoactivated or electroactivated. In those latter cases, the observed luminescence has been attributed to photoreduction processes at the interface between metallic silver and silver oxide leading to the presence of silver clusters [11]. Similar investigations on luminescence of a metallic particle and silver charge aggregate have been carried out in solid state materials [12], [13] and [14]. Yet the origin of the observed luminescence is not clearly identified. In most cases, the involvement of small silver clusters such as Ag_2^+ , Ag_3^{2+} in the vicinity of the surface of larger metallic particles in the luminescence process is hypothesized. However, it is still unclear what mechanisms and structural factors are responsible for the emission of visible light in silver system.

In this paper, we address this problem by investigating the luminescence properties of single colloidal silver nanoparticles. Fluctuations in the emission of the single particles suggest different emission centers and mechanisms. In the mean time, the luminescence

properties of silver colloidal particles and clusters in aqueous polyanion solutions have been investigated. The optical change, both in absorption and emission, which occurs during the Ag^+ silver ion addition onto silver colloidal particles are described. Of particular interest is the interaction of the initially deposited Ag^+ with the underlying silver lattice, how they perturb the optical properties of the silver particles. Initially no fluorescence is observed from colloidal Ag_n . When Ag^+ is admitted to the solution, one finds an intense luminescence in the visible region. Similar luminescence is observed for oligomeric clusters composed of only few atoms. The optical changes observed for $\text{Ag}_n @ \text{Ag}^+$ are interpreted in terms of chemical reorganisation at the surface which leads to the formation of charge oligomeric clusters at Ag_n surface.

2. Experimental section

The radiolytic method employed here for the preparation of the silver colloid solution leads to a well-defined pathway for the reduction of silver ions into charge silver clusters of small nuclearity and colloidal silver particles [15], [16] and [17]. The method allows to produce a known concentration of reducing or oxidizing radicals in the aqueous solution and to let the radicals transfer an electron into the colloidal metal particles. The methods have important advantages in comparison with chemical redox experiments: they are very reproducible, a minimum of disturbing impurities is introduced, and the reactions are initiated homogeneously. Ionizing radiation produces hydrated electrons and hydroxyl radicals. The hydrated electrons are very strong reducing agents which reduce dissolved metal ions, thus produced atoms. The oxidizing OH radicals can be converted into reducing organic radicals in the presence of alcohol:



Thus, by exposing a deaerated silver salt solution ($10^{-4} \text{ mol.l}^{-1}$) containing 0.1 mol.l^{-1} alcohol to γ -rays, the silver is reduced to form colloidal aggregates. A polyanion (10^{-1} – $10^{-3} \text{ mol.l}^{-1}$) in the solution stabilized the aggregates. All reagents were of the highest purity available: silver salt Ag_2SO_4 was from Aldrich, 2-propanol from Prolabo. Milli-Q grade water was used in all the preparations and the reactants. Depending on the conditions, either metallic silver particles of several nanometer in diameter or very small oligomeric clusters are stabilized. All the solutions were prepared in a glass vessel, which carried a sidearm with an optical cuvette. Deaerated NaBH_4 or Ag^+ were added to the Ag sol without exposure to air. The absorption and emission spectra were measured at various times after irradiation to a ^{137}Cs γ source (1.8 kGy.h^{-1}) in a commercial spectrophotometer and spectrofluorimeter. Excitation and emission spectra have been recorded using a system equipped with double monochromators, a xenon lamp for excitation and photomultiplier allowing detection from 200 to 800 nm.

For the single colloidal particles imaging, in order to avoid silver-stabilizer interaction, an alternative method for colloidal metal particles synthesis was used. Silver ions (10^{-3} M) was added slowly in a solution of NaBH_4 (1.5×10^{-3}) under vigorous stirring [18]. Samples prepared by this way exhibit a large size distribution with particles from few nanometers to 50 nm and a large plasmon resonance centered at 430 nm. For single particle imaging and spectroscopy by a scanning confocal microscope, samples were prepared by spin-coating the silver colloids solution on a glass coverslips. Excitation was performed with an Argon ion laser at 476 nm. The laser was focused by 100 \times Oil immersion objective (NA=1.4). Piezo-scanner was used to scan the sample and to position nanoparticles under the focused light. Luminescence of the colloids is sent through a 50/50 beam splitter to a single photon counting module for imaging and on a

spectrometer equipped with nitrogen cooled CCD detector for luminescence spectra recording.

All the particles elaborated were observed in an electron microscope, Jeol instrument (JEM2000FX), operating at 200 kV; samples were prepared by putting a copper-carbon grid on a drop of the solution on oil paper and letting the drop dry almost completely.

3. Results

3.1. Single metallic particle luminescence

Fig. 1 shows a luminescence image from individual silver nanoparticles spin-coated on a glass at atmosphere conditions under blue excitation. Clearly, the different particles display a multitude of colors. The time traces of the light emitted from single nanoparticles display strong intensity fluctuations and blinking (results not shown). Moreover, the luminescence spectra change from particle to particle as clearly shown in Fig. 2a–d. Despite the Raman lines at 515 and 555 nm, for which the positions follow the excitation wavelength, three distinct broad bands around 550, 600 and 650 nm are observed. The relative weight of these bands depends on the silver particle. A time correlated single photon measurement to deduce the luminescence lifetime of single particles has been performed. The results showed a decay time shorter than our instrumental resolution (<38 ps). The luminescence results were compared to those of a bulk sample of silver oxide powder photoactivated at 476 nm (Fig. 2e). The sample exhibits a broad spectrum with multiple components in the whole visible spectrum. Its luminescence is found to increase in time, which is a signature of a continuous formation of emission sites.

3.2. Optical properties of colloidal Ag_n particles in solution

The irradiation of silver ion in the absence of air and in the presence of a polymer leads to silver colloidal particles displaying the well-known Mie resonance around 400 nm (Fig. 3). The wavelength of the plasmon absorption maximum is strongly influenced by chemical modifications of the surface and by an increase of the Fermi level due to a large electron charge density [17]. The spectrum of colloidal silver is altered by addition of borohydride ion in the solution when the reduction of Ag^+ has been uncompleted, since an increase in intensity and a blue-shift in the 400 nm band was observed (Fig. 3b). On the other hand, the deposition of silver ions or oxygen on silver sol completely reduced leads to a red-shift of the resonance plasmon band (Fig. 3c). The changes in the electron density of the particle are reversible and have been used as sensitive indicators for the occurrence of an interaction between the metal particles and a dissolved substrate. Luminescence experiments were carried out on similar silver sol: uncompletely reduced, completely reduced with $NaBH_4$, and subsequently modify with Ag^+ . Whereas an intense and broad emission in the visible (550–750 nm) for excitation at 300 nm for $Ag_n@Ag^+$ or Ag_n uncompletely reduced (Fig. 4), one finds that the luminescence is almost quenched for completely reduced silver sol (not shown). In this latter case, the fairly weak remaining emission at 450 and 650 nm, observed for excitation between 300 to 350 nm, is at the limit of our detection system. It is attributed to the interaction of the carboxyl group of the stabilizing polymer and Ag^+ , since similar weak emission is observed on the solution before γ -rays irradiation. Important change of polymer electronic structure in the presence of silver was already noticed by Mostafavi et al. [19]. The highly intense and broad luminescence observed for $Ag_n@Ag^+$ or uncompletely reduced Ag_n solution display two majors components around 550 and 700 nm. Note that the emission intensity increases with the addition of silver ions with no significant fluctuation of the spectra under our spectral resolution (10 nm). The emission and excitations spectra, shown on Fig. 4, clearly indicate two emission components corresponding to two different excitation wavelength domains. The large emission located around 700 nm corresponds to

excitation wavelengths between 280 to 300 nm; whereas the less intense one around 550 nm appears for excitation in 300–400 nm region. One also finds that the both emission are also observed for excitation in the wavelength domain corresponding to surface plasmon resonance of the silver sol (from 450 to 600 nm). These findings may indicate the presence of two distinct emission centers or one center with complex excited state structure. In addition, since the visible emission is also observed for excitation in the plasmon resonance frequencies of the silver sol, a strong coupling between the Ag_n colloidal particles and the emissive center(s) is expected.

3.3. Optical properties of oligomeric silver clusters in solution

As previously outlined, oligomeric silver clusters can be radiolytically produced in aqueous solution in presence of sodium polyacrylate as stabilizer. The exact nature of the clusters is not fully understood [15]. Nevertheless, pulse radiolysis investigations as well as steady state experiments have given reason for the agglomeration number of the clusters being smaller than 10. The silver clusters, Ag_{4+x}^{x+} and Ag_7^{3+} , have been prepared. They, both, display absorption band at wavelengths shorter than the plasmon band of the larger metallic particles (Fig. 5). The absorption bands from 260 to 350 nm correspond to intrinsic absorption of the clusters, while the large ones respectively around 470 nm for Ag_{4+x}^{x+} and at 580 nm for Ag_7^{3+} are related to the cluster-polymer interaction. The Ag_7^{3+} clusters solution are stable for many weeks, whereas, the Ag_{4+x}^{x+} ones only are stable for few hours. When they disappear, they give rise to larger oligomeric clusters. The color solution turns from pink to blue, characteristic of Ag_7^{3+} clusters. Due to the low stability, we cannot exclude that the shoulder of the absorption spectrum of Ag_{4+x}^{x+} , around 600 nm, correspond to a few larger Ag_7^{3+} clusters. In order to increase the lifetime of the Ag_{4+x}^{x+} clusters and facilitate the optical investigation, an evaporation of the solvent under vacuum was conducted. The resulting material was deposited on fused quartz flakes and further grinded. Despite its stability, a similar process has been applied to the Ag_7^{3+} silver cluster solution to validate the sample preparation. The emission and excitation spectra obtained for Ag_7^{3+} remains identical before and after evaporation.

Fig. 6 reports the emission and excitation spectra of Ag_7^{3+} and Ag_{4+x}^{x+} clusters once deposited. The Ag_7^{3+} solution or deposited on silica flakes exhibit a similar emission centered at 700 nm for excitation around 300 nm (Fig. 6a). This excitation wavelength corresponds to the intrinsic absorption of the silver cluster. In the case of Ag_{4+x}^{x+} clusters, an emission is also observed at 700 nm for excitation around 300 nm while emission at shorter wavelength around 550 nm can be observed for excitation above 300 nm. The excitation band observed either correspond to the absorption band of Ag_{4+x}^{x+} , centered at 280 and 350 nm [19] or to a Ag_{4+x}^{x+} with a few amount of Ag_7^{3+} .

4. Discussion

The ensemble of those results gives new insights in the visible luminescence of silver.

(a) The single particle imaging and spectroscopy experiments suggest that different luminescent centers such as Ag_mO_x clusters (with $m < 10$) are produced from the same single nano-sized Ag_n particles. Indeed, since the luminescence only occurs in the presence of air (not under inert atmosphere), one suggests that a partial oxidation of the silver leads to the formation of Ag_mO_x clusters on the Ag_n surface. Furthermore, the

photoactivation of Ag₂O film leads to the spectrum of Fig. 2e which is overlaying those measured on single Ag_n particles (Fig. 2a–d). The same bands could be distinguished. These observations are in accordance with previously reported study which assigned the emissive sites to small silver clusters (of few atoms) photo-activated by light illumination [20]. Since the photoactivation of Ag₂O produce silver clusters and irradiation of Ag_mO_x on nanometer sized silver leads to similar optical response, one suggests similar origin and sites for the luminescence: Ag_mO_x, Ag_m clusters, coupled with Ag_n particles. The coupling of the particle and the clusters leads to a stabilization of the clusters as well as possible interaction between the plasmon resonance and the clusters luminescence. The short lifetime recorded traduces also such coupling effect. Such shortening of the fluorescence lifetime of dyes or of silver entities at silver particles surface, has previously been observed [21] and [22].

(b) The experiments performed on colloidal and oligomeric silver particles in solution provide more informations on the nature of the emissive centers. In solution, the emission of silver particles is only observed in the presence of silver Ag⁺. The broad emission from 500 to 800 nm with major components, at 550 and 700 nm are observed for an excitation in the UV region or in the surface plasmon resonance. The excitation spectra in the UV region between 270 and 400 nm are close to the absorption of charge oligomeric clusters of small nuclearity, Ag_m^{x+}. In addition, strong similarities exist between the luminescence response of the oligomeric clusters and Ag_n@Ag⁺ sol. Therefore, one suggests that upon addition of Ag⁺ on Ag_n sol, oligomeric clusters Ag_m^{x+} are formed on the surface of the nano-sized metallic particles. The exact nature and size of the oligomeric clusters formed on the surface of the Ag_n sol is still unclear, since the assignment of the emission and the related excitation band is complex. For tentatively evidence the presence of the oligomeric clusters at the surface of the silver sol, Fig. 7 shows the difference between absorption spectra of Ag_n sol after addition of various amounts of Ag⁺ ions (200 μl). The differential spectrum is comparable to the absorption spectrum of oligomeric clusters Ag_{4+m}^{x+} with probably a few amount of Ag₇³⁺, except in 260 nm region. The band in 260 nm region is assigned to the charge transfer band of Ag⁺-polymer. According to those observations, one suggests that optical change accompanying the chemisorption of silver ions to Ag_n particles is regarded to chemical reorganisation of the surface which leads to the formation of oligomeric clusters. The change of electronic properties of the particles earlier studied by Henglein and coworkers is probably not the only cause of optical changes [17]. Quantitative theoretical model for the effect of chemisorption molecules on metal particles is thus highly desirable.

In conclusion, strong luminescence similarities in the visible region are observed from oxidized silver clusters on silver nanoparticles and nano-sized silver particles in solution exposed to silver ion. The coupling effect induces short fluorescent lifetimes of the colloidal silver particles. Comparison with the luminescence of oligomeric silver clusters has been drawn. It is proposed that charge oligomeric clusters Ag_{4+x}^{x+} and Ag₇³⁺ are formed upon addition of Ag⁺ on nano-sized Ag_n particles in solution. The oligomeric clusters are responsible for the strong and intense luminescence observed in the visible region. The luminescence of those nano-objects may offer the possibility of applications for optronics as optical memory elements and in biological labelling. Further investigations are in progress to narrow the size distribution of Ag_n particles and to photo-chemically control the fluorescent spectral features of these coupled systems.

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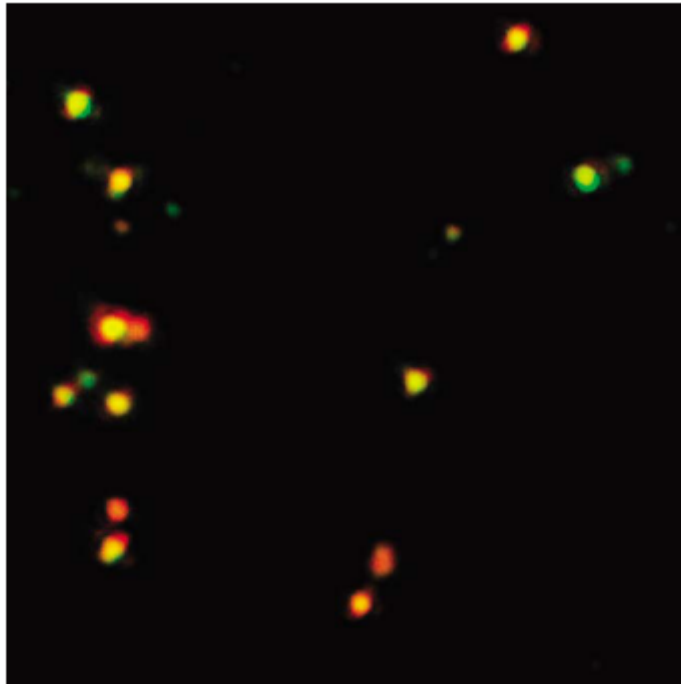


Fig. 1. $10\ \mu\text{m} \times 10\ \mu\text{m}$ luminescence image of silver nanoparticles spin-coated on glass cover slips. The image was taken with Nikon camera within 1 second exposure time. Continuous wave excitation at 476 nm was provided by Ar ion laser. A holographic notch filter (Kaiser Optics) was used to reject the scattered laser light.

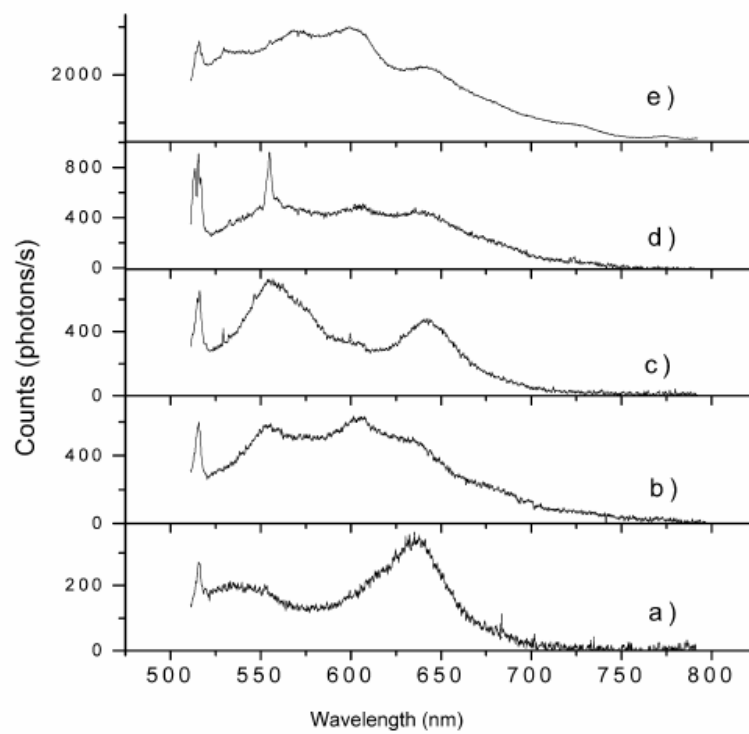


Fig. 2. a)-d): Luminescence spectra of four different single silver particles collected on the same sample. Excitation intensity = $10\ \text{kW}/\text{cm}^2$; integration time = 200 s. e): Luminescence spectrum of silver oxide powder (Aldrich, Purity 99.99%) under laser illumination at 476 nm.

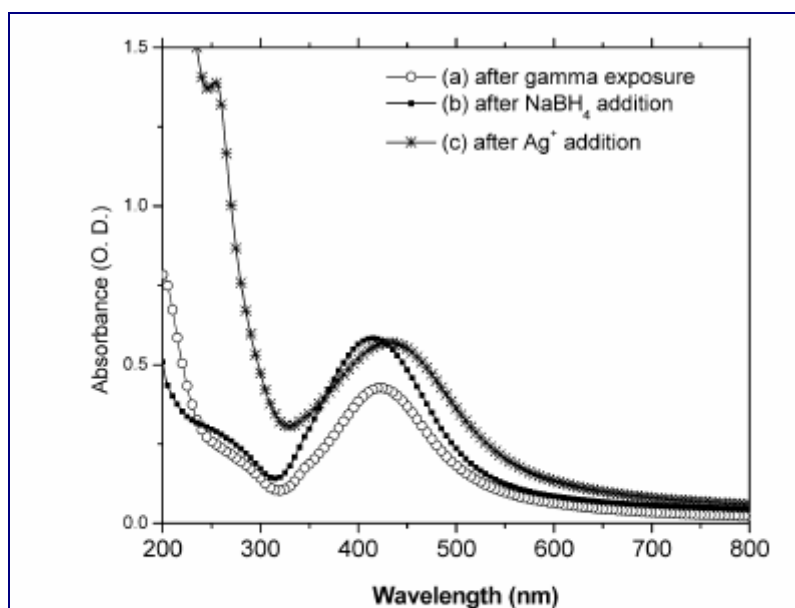


Fig. 3. Absorption spectra of silver colloidal particles. (a) 10^{-4} M Ag^+ solution—uncompleted radiolytical reduction, (b) after addition of NaBH_4 , (c) after addition of 50×10^{-6} M Ag^+ in solution. $[\text{Ag}^+] = 10^{-4}$; $[\text{APA}] = 10^{-2}$ M (MW = 10^4); $[\text{isoOH}] = 0.2$ M; pH = 6.2 (NaOH); irradiation dose: 0.60 kGy. $l = 1$ cm.

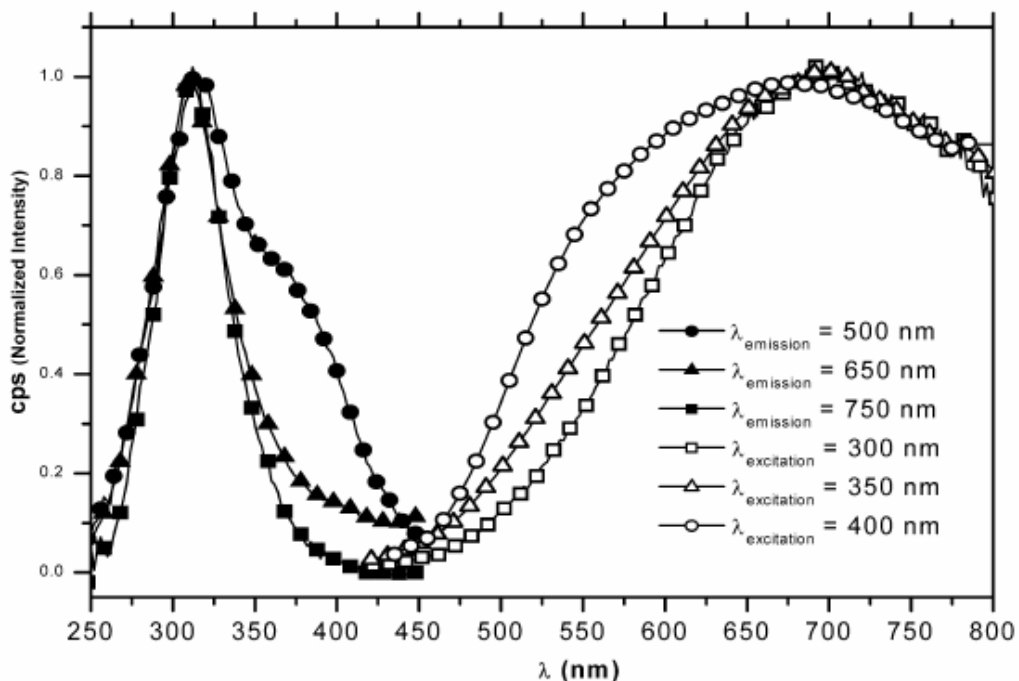
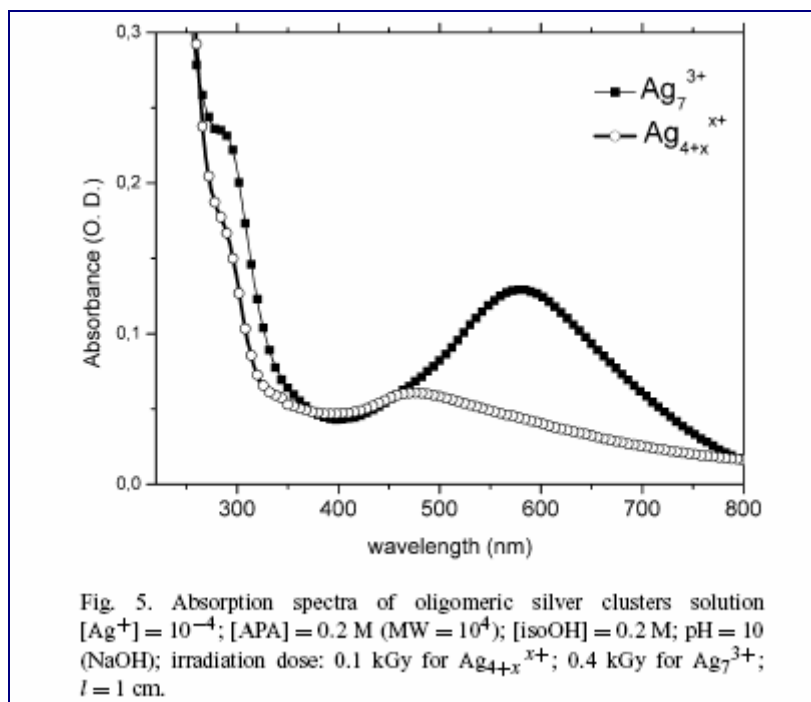
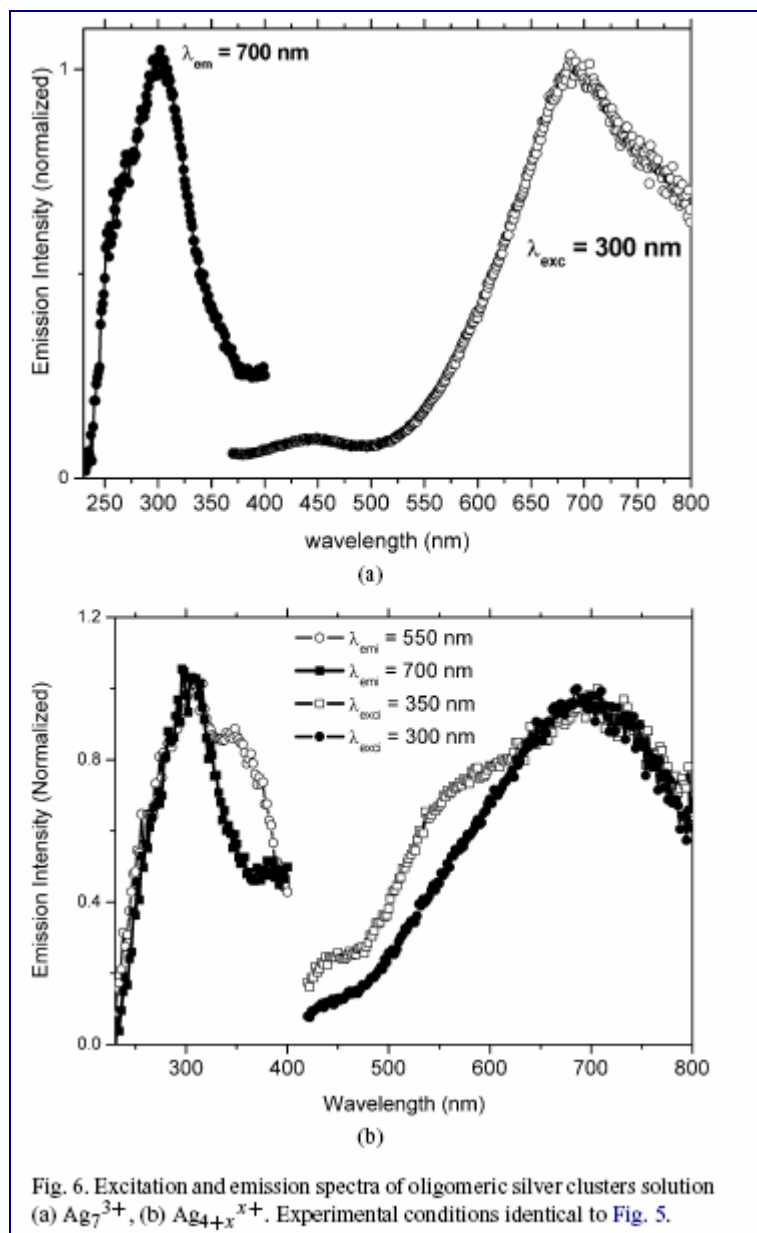


Fig. 4. Excitation and emission spectra of colloidal silver. Experimental conditions identical to Fig. 3.





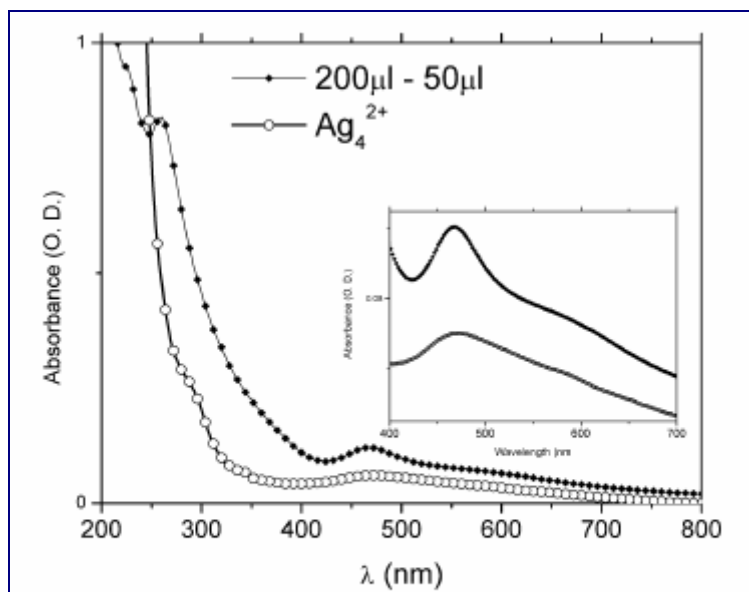


Fig. 7. ■ Absorption spectra difference of silver sol after addition of 200 μl and 50 μl of Ag⁺ ion ($10^{-2} \text{ mol}\cdot\text{l}^{-1}$). ○ Absorption spectrum of Ag_{4+x}^{x+} solution. $l = 1 \text{ cm}$.