# Synthesis of fluorescent silver nanoclusters for environmental sensing applications

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## Abstract

In this work, we synthesized silver nanoclusters (AgNCs) in aqueous phase, with two different capping agents: L-Glutathione (GSH) and polymethacrylic acid (PMAA). In the first case a spontaneous reduction of the $Ag^+$ to $Ag_0$ allows the formation of AgNCs, while in the second one the reduction is induced by UV lamp exposition. We characterized the two systems of AgNCs by Transmission Electron Microscopy (TEM). In both cases, the estimated mean diameter of the nanoclusters is around 2 nm. The systems present optical absorption in the UV-VIS spectral range and they present a strong luminescence, due to their small dimensions. The change of their optical properties in presence of specific heavy metal ions in acqueous solution can potentially be exploited as fluorescent sensor of the presence of dangerous contaminants in water.

## 1. Introduction

Environmental contaminants are becoming an increasingly serious problem due to the many industrial activities all over the world. Large quantities of chemicals used in agriculture, industry and daily life are discharged into the environment with consequent contamination of air and water. In order to protect habitat security and human health, it is extremely important to develop devices, which are able to detect the presence of pollution. Currently, various complicated test methods are used, including atomic absorption spectroscopy, fluorescence spectroscopy, ion chromatography, etc., but these analytical tools are expensive, time spending, materials consuming and well-trained operators are necessary for the analisys[1-3].On the contrary, simple optical devices are cheap and easy to synthetize and indeed, they have been already used to detect different types of environmental contaminants, such us heavy metal ions[4,5] or volatile organic compounds [6,7].

In the last decade, nanomaterials have attracted the scientific community for their unusual features with respect to the same bulk material. Among the most studied nanomaterials, there are metal nanoclusters (MNCs), with a mean diameter below 2 nm which consist of tens of metal atoms. Differently by the bulk metal and metal nanoparticles (MNPs, mean diameter greater than 2 nm), where electrons can move freely in all volume (bulk metal) or on the surface (MNPs), metal NCs have discrete energy levels and their behaviour are ruled by quantum mechanics. This behaviour confer them very interesting physical and chemical properties[8]. Due to the presence of discrete energy levels, electrons are confined to move on these levels, producing only electronic transitions, from a fundamental state ($E_0$) to an excited state ($E^*$) as in case of atomic and molecular radiative de-excitations. For this reason, MNCs can show a very intense luminescence. The figure 1 shows photographs of three different systems under daylight (left side) and under UV light (right side). The system named (1) is a colloidal suspension of silver nanoparticles (AgNPs, with mean diameter of 4 nm)[4], the solution is yellowish and it does not show any photoluminescence. The system labelled (2) is a colloidal water solution of AgNCs capped with GSH, under white light it is transparent and clear, under UV radiation shows a bright blue luminescence. The system called (3) is an AgNCs solution stabilized with PMAA, it is orange under visible light and displays a red luminescence when illuminated with an UV lamp.

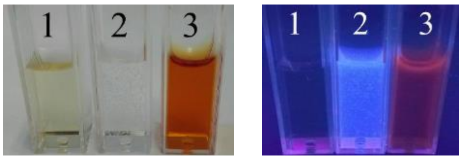


Fig. 1 Photographs of three colloidal solutions: (1) AgNPs, (2) AgNCs stabilized with GSH, (3) AgNCs capped by PMAA. Left side: solutions are under white light; right side: solutions are under UV light. Only AgNCs systems show luminescence.

## 2. Experimental Results and discussion

*2.1 Materials*

Silver nitrate ($AgNO_3$), reduced glutathione (GSH), polymethacrylic acid sodium salt solution (PMAA, concentration of 30% in wt, $M_w$ = 9500), sodium hydroxide (NaOH) and nitric acid ($HNO_3$) were purchased from Sigma-

Aldrich and were used as received without further purification. All reagents were dissolved in deionized water.

*2.2 Silver nanocluster capped with GSH*

In a typical synthesis, we used 1,5 ml of $AgNO_3$ water solution with a concentration of 20 mM (Solution 1), freshly prepared; 6 ml of GSH water solution with a concentration equal to 50 mM (Solution 2). All steps of the synthesis are carried out under a yellow lamp, because $AgNO_3$ is sensible to UV light. Solution 2 is placed into a beaker under vigorous mechanical stirring, this is a very clear and transparent solution. Subsequently, we added drop by drop the Solution 1 and suddenly the mixture turns to opaque. This change is referred to as the formation of Ag-GSH complexes that are insoluble in water (initial pH = 2). To increase the solubility, we added some drops of NaOH (1M) to change the pH value up to 5. At this stage, the solution changes its aspect to transparent and clear indicating that Ag-GSH complexes are completely solubilized [9,10] and very small particles are formed. After the synthesis the solution is stored in the dark at T = 4°C.

*2.3 Silver nanocluster capped with PMAA*

In the case of AgNCs capped with PMAA (Ag-PMAA), we started from an $AgNO_3$ water solution with a concentration of 50 mM and the concentration of capping agent is chosen to have a molar ration between carboxyl groups and $Ag^+$ equal to 1:2, according to maximize the luminescence emission [11, 12]. The $Ag^+$ solution was mixed with the PMAA solution and the pH was adjusted up to 4.5 by adding $HNO_3$. After, the aqueous mixture is exposed to UV lamp (300 W, NEWPORT, Oriel Instruments U.S.A.) to reduce $Ag^+$ to $Ag_0$ [12, 13], in presence of a nitrogen flux to prevent the oxidation of surface solution of AgNCs.

*2.4 Experimental apparatuses*

We have characterized AgNCs solutions by optical absorption and fluorescence spectroscopy. Absorption spectra were recorded with a *Perkin-Elmer Lambda 19* spectrometer in the range of 300-700 nm. Luminesence spectra of the solutions in quarts cuvettes were collected by an optical fibre (*OceanOptics, QP600-2UV-BX*) connected with an *OceanOptics Flame* spectrometer. Excitation wavelength was at 364 nm with an $Ar^+$ Laser (*Coherent*, *Innova 90C*). Photoluminescence spectra are recorded in the range 350-1100 nm. The morphological characterization of the AgNCs has been accomplished with a Transmission Electron Microscope (TEM). The experimental apparatus is a FEI TECNAI 12 G2 (120 KeV) equipped with an energy filter (GATAN GIF model) and a Peltier cooled SSC (slow scan charged coupled device) multiscan camera (794 IF model).

## 3. Results and discussion

In Figure 2 are reported the TEM images of the two systems: Ag-GSH NCs and Ag-PMAA NCs. The dimensions of both systems are of about 2 nm. In the case of NCs capped with glutathione, from the low resolution images (not shown here) filaments of glutathione incorporating silver nanoclusters appear. This behaviour prevents the aggregation of NCs, giving to the system excellent optical properties as shown in the next. The shape is quite spherical and we estimated the mean diameter by TEM images, which is 2.4 ± 0.8 nm. Differently, in the case of Ag-PMAA (Figure 2(B)), NCs and no filaments are observed and the NCs appear are more dispersed with respect to the other synthesis. From TEM images, we calculated the average size of Ag-PMAA that is 1.6 ± 0.3 nm. The the shape, also in this case, is spherical and the size distribution is narrower than the GSH stabilized NCs.

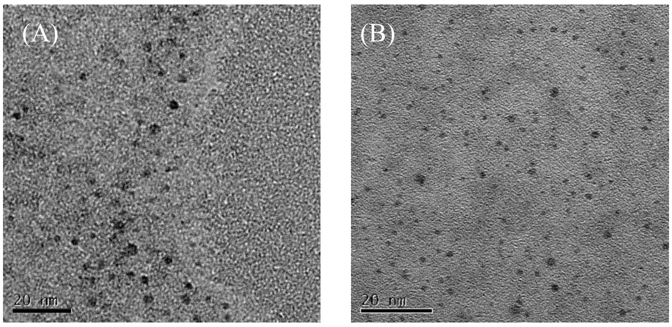


Fig. 2 TEM images of two systems: Ag-GSH nanoclusters(A) and Ag-PMAA nanoclusters (B).

Figure 3 reports the absorption (solid black curve) and the luminescence (solid red line) of the Ag-GSH NCs solution. The absorption band maximum is centred at wavelength of 350 nm and the Full Width at Half Maximum (FWHM) of about 20 nm, is very narrow for a system in liquid phase confirming the very high monodispersion of the NCs analyzed with TEM characterization. The maximum wavelength of the emission is at 450 nm, when the system is excited with 364 nm laser line.
We tried to promote the reduction of $Ag^+$ to $Ag_{0,}$ by sonication or UV exposure of the Ag-GSH solution. We the optical absorption of three samples of Ag-GSH NCs monitored as a function of time after the synthesis. The first one, without any further treatments (UV or sonication), it is our reference sample; the second one is exposed under UV lamp (sample n° 1); and the last one is treated with ultrasonic waves at 40 kHz (sample n° 2). The figure 4 shows optical absorptions of the three samples after 45 minutes of treatment. Solid black line represents the spectrum of colloidal suspension just synthetized (reference at t = 0 minutes), solid red curve is the reference at t = 45 minutes; the dotted blue curve corresponds to 45 minutes of UV exposure (sample n° 1), finally, the dashed green line symbolized the 45 minutes of ultrasonic treatment (sample n° 2). The UV irradiation (sample n° 1) does not promote the formation of NCs, actually, it degrades the already existing nanoclusters or the capping agent and the characteristic peak of the absorption spectrum decreases together with a slight increase of the scattering of light for longer wavelength. In addition, the colour of sample n° 1 changes to dark red from colourless solution after the UV treatment. After 45 minutes of sonication (sample n° 2), the intensity of the band increases with respect to the reference and the scattering decreases indicating that such treatment promotes the birth of new NCs. At naked eye, the aspect of the solution remains the same (colourless).

Absorption and luminescence spectra of colloidal solution of Ag-PMAA NCs are shown in Figure 5. The solid blue line represents the optical absorption of silver and capping agent solution before the UV irradiation. In this case, the absence of structural features indicates the absence of NCs. This solution does not exhibit any detectable luminescence. In order to produce the formation of the silver NCs, we exposed the solution to an UV lamp for 6 minutes. After the exposition, the absorption shape changes with the appearance of a small band at around 420 nm (solid black line) which indicates the formation of Ag-PMAA NCs. The relative luminescence (solid red line in figure 5) excited at 364 nm presents a maximum at about 640 nm.

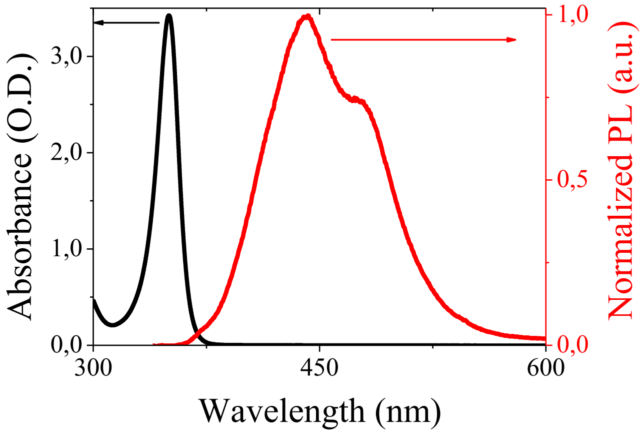


Fig. 3 UV-Vis absorption spectrum of Ag-GSH nanoclusters (solid black line); photoluminescence spectrum of Ag-GSH NCs excited at 364 nm (solid red line).

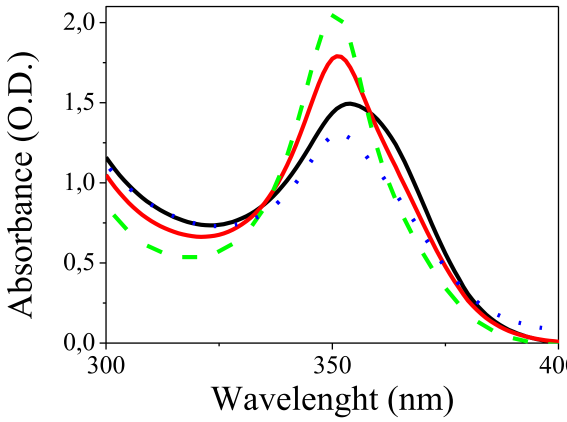


Fig. 4 UV-Vis absorption spectra of the reference (no treatment), sample n° 1 (UV irradiation) and sample n° 2 (sonication), as function of treatment time. The solid black line corresponds to the reference sample at t = 0 minutes. Coloured curves symbolize the reference (solid red curve), the sample n° 1 (dotted blue curve) and the sample n° 2 (dashed green line) after 45 minutes of treatment.

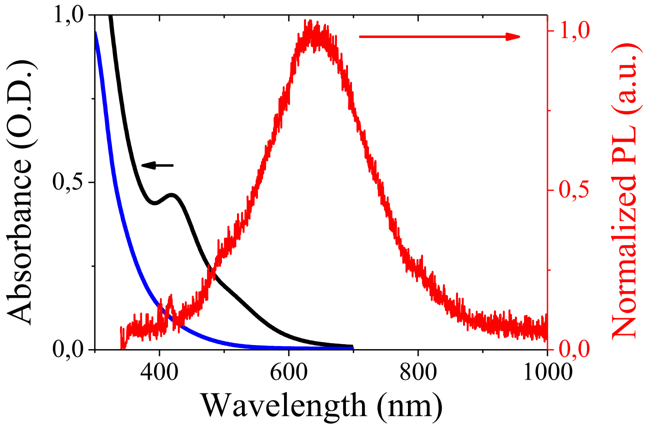


Fig. 5 UV-Vis absorption spectra of Ag-PMAA nanoclusters, before UV exposure (solid blue line) and after 6 minutes of UV irradiation (solid black curve); normalized photoluminescence spectrum of Ag-PMAA NCs excited at 364 nm (solid red line).

Photoluminescence is a very interesting optical property that can be used in many applications such as fluorescent label in biological systems or as optical sensors. In general, the luminescence is more sensible than absorption to the presence of contaminants in certain systems. On this regard, we started to investigate the luminescence spectra of both systems, Ag-GSH and Ag-PMAA, in presence of heavy metal ions such as As(III), $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$. These preliminary measurements show that the presence of certain metal ions can modify the luminescence spectrum, thus, laying the foundations for the development of optical sensors in environmental field. Future studies will be lead to investigate these aspects.

## 4. Conclusions

We synthetized small silver NCs (mean diameter of about 2 nm) stabilized with two different capping agents such as GSH and PMAA. Ag-GSH NCs present an optical absorption at 350 nm while Ag-PMAA NCs have a maximum peak at about 420 nm; moreover, the two systems have different photoluminescence when excited at 365 nm: at 450 nm and at 640 nm for GSH and PMAA stabilized NCs, respectively. From preliminary results we found a change of the luminescence intensity of these systems when heavy metal ions are inserted in the solutions. These results are very promising and could be potentially exploited for the development of specific devices able to monitor the presence of such contaminants in water.

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