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# Synthesis of Fluorescent Silver Nanoclusters with Potential Application for Heavy Metal Ions Detection in Water

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**Abstract.** Metal nanoclusters (MNCs) are small aggregates of metal atoms with a mean diameter up to 2 nm, that when excited by electromagnetic radiation of suitable energy present an intense florescence. This optical property can be exploited in many fields such as bioimaging, drug delivery and optical sensing in environmental monitoring. In the present work, we synthesized silver nanoclusters (AgNCs) in water starting from $AgNO_3$ and exploiting poly (methacrylic acid) (PMAA) as capping agent. The reduction of the silver ions Ag(I) to Ag(0) was promoted by the exposition of the solution to UV light radiation for 6 minutes. We studied the UV-Vis absorption and the fluorescence spectra for different pH values. The morphological characterization of the solution was accomplished by Transmission Electron Microscopy (TEM) and the statistical analysis showed that the mean diameter of the AgNCs was around 2 nm for the solution at pH = 4 which presented also the strongest fluorescence. Moreover, we studied the time stability of the absorption and fluorescence spectra. AgNCs stored in the dark at 4 °C were stable for more than 60 days. A possible application of the synthesized AgNCs deals with water monitoring by optical sensing based on the change of the fluorescence property in presence of heavy metal ions. Preliminary investigations show a high sensitivity to Pb(II) ions.

## INTRODUCTION

Nanomaterials showing peculiar optical properties such as absorption and fluorescence have attracted the interest of researchers in many application fields of science. Semiconductor quantum dots (QDs), such as CdSe, CdTe, PbSe, InP, InAs and GaAs [1–3], present a broad excitation range, a narrow emission peak ranging from UV to NIR and high resistance to photobleaching. These characteristics have been largely exploited for biological [4,5], sensing [6–8] and imaging [9–11] applications. Upconversion nanomaterials, which are compounds converting the low-energy excitation light to higher-energy emission light through sequential absorption of multiple photons or energy transfer [12], are promising fluorescent species in chemical sensing [13,14] and bioimaging field [15,16]. Graphene or graphene oxide quantum dots are fluorescent material with many applications for chemical and biological sensing [17–19], bio-imaging [20,21] and drug delivery [22]. Metal nanoparticles (NPs) having a sharp absorption band related to the localized surface plasmon resonance are good candidates for applications in energy [23–25], optoelectronics [26,27] and sensing [28–31].

Metal nanoclusters (MNCs) have attracted much interest in the last years as stable and highly fluorescent material. MNCs are agglomerates of few tens of metal atoms (gold, silver or platinum) having a size which is comparable to Fermi wavelength of one electron and for this reason present a molecular-like behavior. Thanks to the very small diameter (below 2 nm), MNCs show a bright fluorescence due to the quantum confinement effect of the metal electrons [32,33]. Such an intense fluorescence finds interesting applications in bio-labeling [34,35] and imaging [36,37]. Moreover, since the MNCs fluorescence is very sensible to the external environment and to the

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presence of contaminants, an interesting field is those related to the optical sensing [38–40]. The attention to the environment quality is becoming always more important since the environmental poisoning by dangerous substances is growing continuously. In particular the contamination by heavy meal ions, which are not biodegradable and accumulate in the soil and in the water and as a consequence they can contaminate also food and water [41]. The exposure to heavy metal ions can create disease and pathology [42,43]. For these reasons, easy and low cost methods of heavy metal ions detection such as those based on the change of optical features (absorption or luminescence) are highly desirable. MNCs are promising candidates to be successfully used to detect heavy metal ions in water [44–46].

In this work, we synthesized AgNCs by photoreduction exploiting UV radiation. The nanoclusters were capped with poly (methacrylic acid), PMAA and the effect of the pH (from 1 to 8) was investigated. The stability of the NCs as a function of the time was evaluated. The fluorescence properties were investigated and the solution with pH equal to 4 presented the higher fluorescence intensity. By Transmission Electron Microscopy (TEM) analysis, we investigated the morphology of the NCs finding a mean diameter of 1.9 ± 0.8 nm for a pH value equal to 4. Preliminary investigations about heavy metal ions sensing based on a change of the fluorescence intensity are reported and Pb(II) ions in water presented the highest optical response.

## EXPERIMENTAL SECTION

### Materials and Methods

Silver nitrate ($AgNO_3$), polymethacrylic acid sodium salt solution (PMAA, concentration of 30% in wt, Mw = 9500), sodium hydroxide (NaOH) and nitric acid ($HNO_3$) were purchased from Sigma Aldrich and were used as received without further purification. We started from an $AgNO_3$ water solution with a concentration of 50 mM and the concentration of capping agent was chosen to have a molar ratio between carboxylate groups and Ag(I) equal to 1:2, according to literature [47]. The two solutions were mixed together and the pH was adjusted to the desired value adding $HNO_3$ or NaOH. Solutions with pH in the range (1-8) were produced. The AgNCs were produced by a photoreduction process consisting in the UV radiation exposition of the solutions. All the samples were exposed for 6 minutes to UV lamp (300 W, NEWPORT, Oriel Instruments U.S.A.), to promote the reduction reaction of silver ions (Ag(I)) to silver metal (Ag(0)). Finally, we fluxed nitrogen gas onto the solution surface to hamper the oxidation of growing NCs. After synthesis, the solutions were stored in the dark at 4°C. We tested the optical response of AgNCs to some metal ions such us As(III), Cd(II), Cu(II), Na(I), Pb(II) and Zn(II). The used salts were: sodium (meta)arsenite [$NaAsO_2$], cadmium nitrate pentahydrate [$Cd(NO_3)_2 \cdot 5H_2O$], copper nitrite pentahydrate [$Cu(NO_3)_2 \cdot 5H_2O$], sodium chloride [NaCl], lead nitrate [$Pb(NO_3)_2$] and zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$]. All reagents were dissolved in deionized water (MilliQ water). The optical characterization of the AgNCs was performed by UV-Vis absorption and photoluminescence (PL) spectroscopy. Absorption spectra were recorded with a Perkin-Elmer Lambda 19 spectrometer in the range of 200 -700 nm, using quartz cuvettes of 1 mm. For sensing tests a classical luminescence investigation apparatus with a 90-degree geometry, made up from Hg(Xe) discharge lamp (Orel instruments, Stratford, CT, USA) an excitation 25-cm monochromator (Photon Technology International, INC., Birmingham NJ, USA), a specimen, an emission 25-cm monochromator (Cornerstone 260, Stratford, CT, USA) and a photomultiplier (Hamamatsu Photonics Corp., Bridgewater, NJ, USA) as detector [48,49]. The excitation wavelength was 340 nm. The morphological characterization of the AgNCs has been carried out with a Transmission Electron Microscope (TEM) apparatus (Thermo Fisher Scientific, FEI, TECNAI 12 G2 (120 KeV)) equipped with an energy filter (GATAN Biofilter model GIF) and a Peltier cooled SSC (slow scan charged coupled device) multiscan camera (794 IF model).

## RESULTS AND DISCUSSION

Absorption spectra of the solutions with different pH from 1 to 8 are reported in Figure 1(a). For pH in the range 1-4 no peculiar features are present in the absorption spectra confirming the presence only of NCs. The wide band from about 410 nm to 600 nm (for pH range 6-8) indicates the presence of very large diameter silver aggregates as indicated also by the large background of the curve that can be ascribed to the light scattering. For pH 4.5 and 5 the large band disappears and a shoulder around 420 nm appears. This band has been assigned to the surface plasmon resonance related to presence of nanoparticles with mean diameter larger than 2 nm [50,51]. Decreasing the pH until 1, there are no structures in absorption spectra. The solutions under visible light show an impressive color change from black to pale yellow changing the acidity of the solution from basic to acid conditions, respectively (Figure 1(b)). In Figure 1(c) a photograph of the same solutions but under UV light exposition is reported. The orange fluorescence is clearly visible, even by naked eye, for the solutions having pH in the range from 5 to 2 of pH values with a maximum of intensity for pH equal to 4. Different values of acidity of the synthesis strongly affect the interaction between polymer chains and silver ions and the PMAA chains conformation. For pH values below 6 the PMAA functional groups are protonated and as a consequence, the conformation of the polymer is in a compact structure. On the contrary, if the pH is greater than 6, the polymer chains present charged –COO$^-$ groups, which repelling one each other produce a polymer conformation that is relaxed [52]. These aspects could influence the AgNCs growth, determining various mean diameters as function of the acidity.

The PL spectra present a well-shaped band in the orange-red visible spectral range and the band maximum shows a slight dependence on the pH value. In Figure 2(a) normalized PL spectra for pH values of 3 (black line), 4 (red line) and 5 (blue line), are reported. The peak position spectra show a slight wavelength shift indicating a change in the average dimension of AgNCs: the greater the number of atoms for each cluster, the lower the emission energy, as reported in the literature [32,53]. In Figure 2(b) the intensities of the PL of different solutions as a function of the pH are reported. The solution with pH = 4 presented the highest PL intensity indicating that under this condition a maximum number of luminescent AgNCs are produced with a low presence of big nanoparticles and silver NPs aggregates. This behavior is confirmed by TEM analysis. The Figure 3(a) shows a TEM image of the solution having pH = 4 where a large number of well-separated small silver nanoclusters can be appreciated. After a statistical analysis on about 100 nanoclusters, we estimated a mean diameter of 1.9 ± 0.8 nm as reported in Figure 3(b). A good monodispersion of the system can be appreciated since only 4 particles, on about 100 NCs analyzed, presented diameter greater than 3.6 nm. Such a small average dimension ensures an adequate quantum confinement of electrons in the nanoclusters and as a consequence an intense luminescence as measured in our samples.

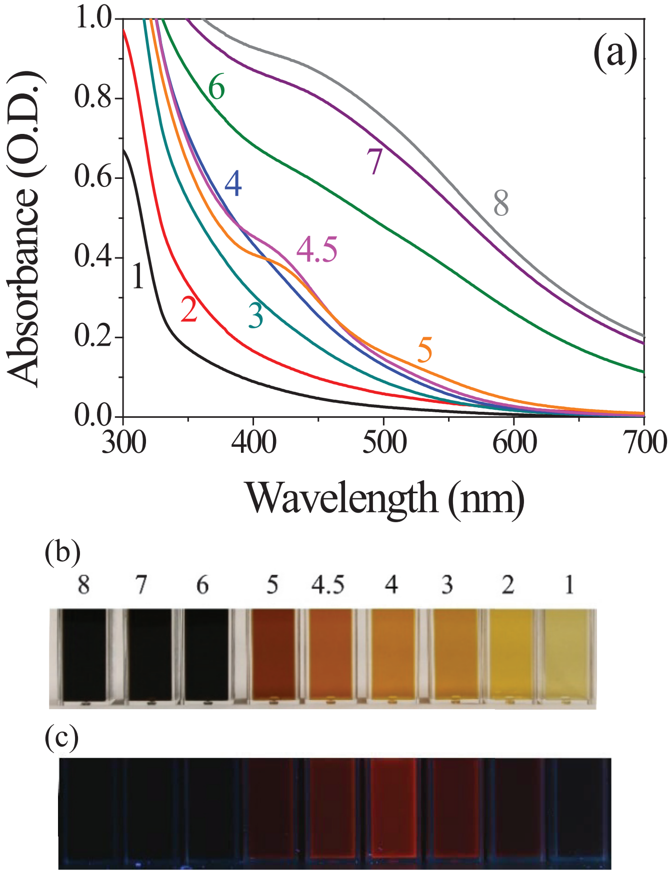

**FIGURE 1.** (a) Optical absorption in the UV-Vis range, for solution at different pH; photographs of samples at different pH values: (b) under white light; (c) under UV light.

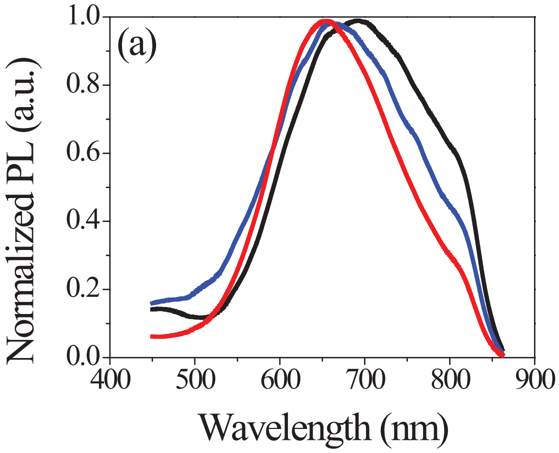

**FIGURE 2.** (a) Normalized PL spectra for solutions with pH value of 3 (black line), 4 (red line) and 5 (blue line); (b) PL intensity for solutions having different pH values (the scale is normalized to the maximum of the signal at pH=4).

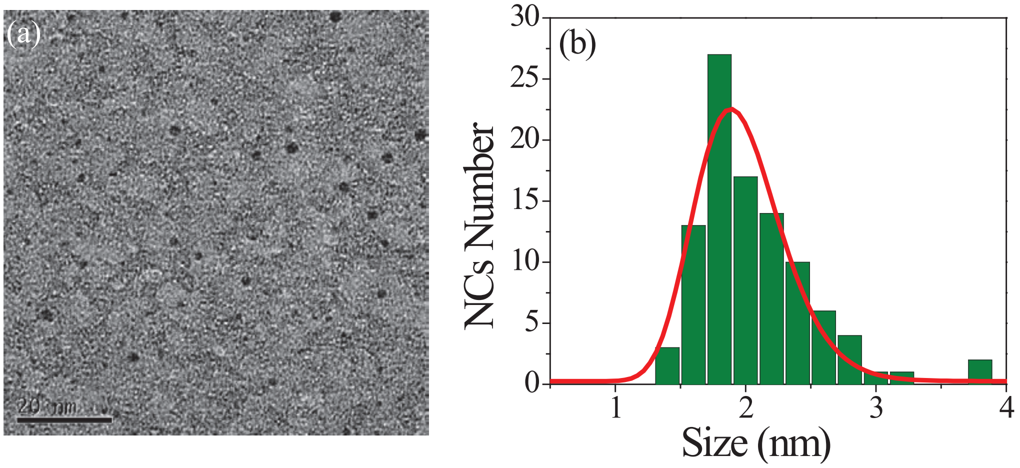

**FIGURE 3.** (a) TEM image of AgNCs capped with PMAA, at pH = 4; (b) statistical analysis of the AgNCs distribution.

The AgNCs solutions are stable as a function of time if stored at T = 4°C and in the dark. We measured the absorption and luminescence properties for more than two months. In the indicated time interval, no differences in the absorption features were recorded as well as in the luminescence signals as reported in Figure 4.

As a final step, we tested the change of the absorption and luminescence properties of the AgNCs solution (pH = 4) in presence of heavy metal ions in order to test the sensibility of the silver nanoclusters to specific contaminants. The optical absorption did not show any remarkable difference before and after the adding of metal ions salt solution in the AgNCs solution while the luminescence presented interesting changes regarding the intensity without a substantial difference in the band shape. Indicating with $F_0$ and F, respectively, the maximum intensity of PL emission of the AgNCs without any contaminants and in presence of each metal ions, we plotted the ratio $F/F_0$ as a function of the contaminant species in the histogram presented in Figure 5. For this preliminary investigation, we tested the optical response of AgNCs to As(III), Cd(II), Cu(II), Na(I), Pb(II) and Zn(II). All the contaminants were tested for two concentrations: 100 μM (blue bars) and 50 μM (red bars). In the case of As(III), Cu(II) and Na(I) no significant changes of the PL emission were measured, while for Cd(II) and Pb(II) (and only slightly for Zn(II)) an enhancement of the PL signal was detected. In particular, the intense PL enhancement induced by the presence of lead ions (relative increase of the PL was about 90% for 50 μM concentration) seems very promising for Pb(II) detection in water solutions at low concentrations. Further characterization and optimization of AgNCs capped with PMAA are currently under investigation in order to improve the sensing properties of such system.

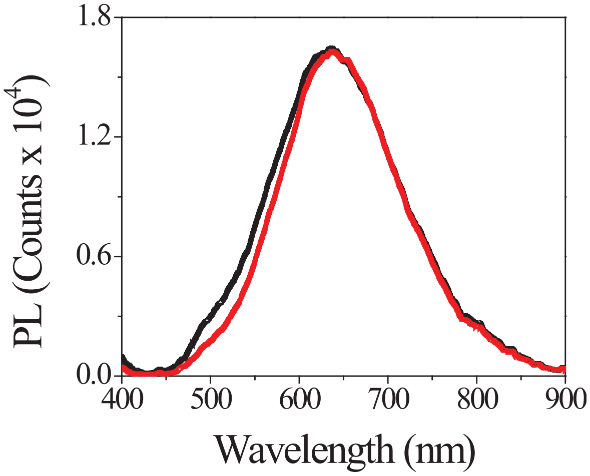

**FIGURE 4.** Time dependence of the PL intensity of the AgNCs solution (pH = 4). Black curve is the PL spectrum immediately after the synthesis, while the red curve is the PL spectrum after 62 days.

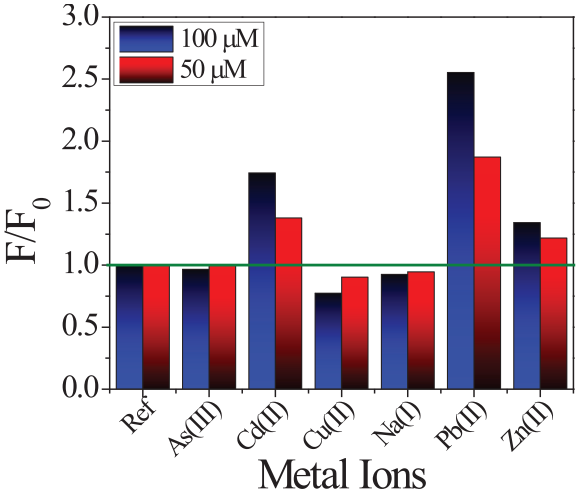

**FIGURE 5.** Relative AgNCs PL intensity in presence of some heavy metal ions at concentrations of 100 µM (blue bars) and 50 µM (red bars).

## CONCLUSIONS

In this work, we reported a successful method to synthesize a very stable colloidal water solution of silver nanoclusters capped with PMAA exhibiting a strong fluorescence depending on the pH value. By TEM analysis, we estimated an average diameter of the AgNCs equal to 1.9 ± 0.8 nm at the pH = 4 with a high degree of monodispersity. We tested the optical response of the colloidal solution to some heavy metal ions. In particular, an interesting fluorescence enhancement in the presence of Pb(II) was found. These preliminary results are encouraging for the use of AgNCs capped with PMAA in the heavy metal ions detection field.

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