

Silver Nanoparticles with Different Thiol Functionalization: An Opposite Optical Behaviour in Presence of Hg(II)

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Abstract. We synthesized two different functionalized silver nanoparticles (AgNPs) in water, starting from silver nitrate, as Ag(I) ions precursor, and sodium borohydride, as reduction agent. The first system was capped with sodium 3-mercapto-1-propansulfonate (3MPS), while L-Cysteine and citrate stabilized the other system. We characterized both systems by UV-Vis absorption spectroscopy and transmission electron microscopy (TEM). We tested their optical response to several heavy metal ions monitoring the Localized Surface Plasmon Resonance (LSPR) band. In particular, these two systems have an opposite optical behaviour in presence of Hg(II) ions as contaminants. In the case of AgNPs-L-Cysteine/citrate, the plasmonic band shifted to higher wavelengths affording a linear behaviour and LOD, in the range from 1 to 7.5 ppm and 600 ppb, respectively; whereas, the AgNPs-3MPS peak shifted to lower wavelengths with a linear range from 0 to 5 ppm and a LOD of 240 ppb for Hg(II). A preliminary hypothesis about the interaction mechanism between AgNPs and Hg(II) ions is discussed.

Introduction

Micro and nano-materials, display unique physical and chemical properties with respect to the same materials in bulk structure. These particular features are widely exploited in numerous fields, such as energy, optoelectronics, biomedicine and sensors[1–9]. In the field of sensors, optical properties can be based on reflectivity, photoluminescence emission and absorption of micro/nano-systems. When certain contaminants, such as small molecules, volatile organic compounds (VOCs), pesticides or heavy metal ions (HMIs) interact with the optical device, they are able to change the optical signal on which the sensor is based. In general, the variation of the signal can regard its intensity, its energy or its shape. These changes are related to the different nature of the interaction between the optical device and the external stimulus.

Among sensors based on light reflection, photonic crystals (PCs) show a Bragg-like diffraction in the visible range as a consequence of a peak in the reflectance spectrum[10–12]. The porous structure of PCs allows the permeation of contaminants between the spheres and a

change of dielectric function of the whole device occurs causing a shift of the reflectivity band. Sensors based on PCs have been employed for the detection of several hazardous compound such us VOCs[13–16].

Although inorganic quantum dots (QDs), graphene oxide quantum dots (GOQDs) or metal nanoclusters (MNCs), have different chemical structures and are obtained with different synthetic strategies[17–22], they are linked by a common feature: the photoluminescence emission (PL). Also, in these cases, photoemitting material have been used to detect the presence of various species of pollutants[23–28]. The interaction mechanism would explain the opposite behaviour in the PL intensity change[29].

Among the sensors based on a change in optical absorption[30–32], metal nanoparticles (MNPs) show a typical absorption peak in the UV-Vis range, due to the phenomenon of Localized-Surface Plasmon Resonance (LSPR)[33]. To prevent the aggregation of these MNPs, during the chemical synthesis, a stabilizing molecule, which is also a species sensitive to the presence of the pollutants, is introduced. Colloidal solutions of MNPs show a specific colour depending on the type of noble metal (gold, silver or copper), on the size and shape of the NPs[34], thus a shift of the plasmonic band produces a change of colour of the solution, which can be appreciated by naked eye (colorimetric sensors)[35–38]. The study and the development of optical sensors should be encouraged for the simplicity of the synthesis, the fast response to the external stimulus and the ease of data interpretation.

In this work, two different AgNPs systems functionalized with hydrophilic capping agents were synthesized, using citric acid (Cit) and L-Cysteine (L-Cys) for the first Ag-nanosystem and 3-mercapto-1-propanesulfonate (3MPS) for the second one. We characterized both systems, by Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM) analysis confirming nanosized dimensions. AgNPs- 3MPS and AgNPs-L-Cys/Cit were tested as plasmonic sensor for heavy metal detection in water, showing a good response for Hg(II) ions in both cases, but with an opposite behaviour. A hypothesis about the interaction mechanism between AgNPs and Hg(II) ions were discussed.

Experimental section Chemical reagents

Silver nitrate (AgNO_3), Sodium borohydride (NaBH_4), Sodium 3-mercapto-1-propanesulfonate (3MPS), Sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Cit), L-Cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$, L-Cys) have been purchased from Sigma-Aldrich. For the sensing tests we used the following metallic salt: NaAsO_2 , $\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, KClO_4 , $\text{Mg}(\text{ClO}_4)_2$,

NaClO_4 , $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ purchased from Sigma-Aldrich. All chemical reagents have been used as received without any further process and all solutions have been prepared with deionized water (resistivity $18.2\text{M}\Omega\text{cm}$ at 25°C) obtained from Millipore Milli-Q water purification system.

Apparatus

Optical characterizations of bare AgNPs systems and contamination tests have been performed by Perkin-Elmer Lambda 19 UV/Vis/NIR spectrophotometer, in the range from 300 nm to 700 nm. The morphological characterization of the AgNPs 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).

Synthesis of AgNPs

The AgNPs stabilized by 3MPS were prepared by a wet reduction of AgNO_3 with NaBH_4 . The detailed synthesis is reported in our previous works [39,40]. Briefly, the AgNO_3 water solution is added dropwise to NaBH_4 solution under vigorous stirring at the temperature of 3°C ; 3MPS was subsequently added and it capped the silver nanoparticles. After the synthesis is completed, the solution is stored at $T = 4^\circ\text{C}$ before the analysis.

The AgNPs stabilized with citrate and L-Cysteine were prepared and characterized in analogy to literature reports [41–43]. Sodium citrate, L-Cys and AgNO_3 were dissolved separately in distilled water and then the three solutions were mixed under magnetic stirring. After degassing the mixture with Argon for 10 minutes, a NaBH_4 solution were added and allowed to react at room temperature for 2 hours. The obtained brown solution was purified by centrifugation, collecting the AgNPs in the precipitate and resuspended in water (13000 rpm, 10 min, 2 times with deionized water).

Results and discussion

Fig.1 shows a TEM image of the AgNPs-3MPS system: the particles have a mean diameter of about 4 nm. The dimensional characterizations obtained by TEM analysis for both systems are listed in Table 1

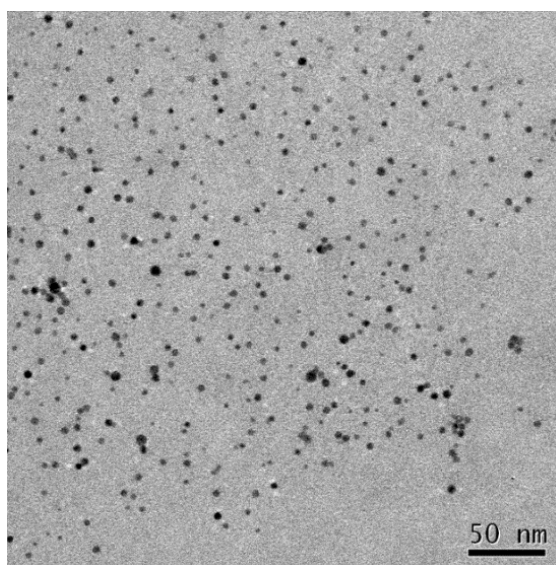


Fig. 1. TEM image of the AgNPs-3MPS system.

Fig. 2 shows the optical absorption in the UV-Vis range for both AgNPs systems. The solid black line represents the AgNPs-3MPS solution; the plasmon band absorption has the maximum centred at 396 nm and a Full Width at Half Maximum (FWHM) of 74 nm. The green dashed curve is the absorption of the reference solution of AgNPs- L-Cys/Cit, in this case the maximum of the peak is at 401 nm and the FWHM is 102 nm.

Table 1. TEM size comparison.

System	Size by TEM	REF.
AgNPs-3MPS	4.1 ± 0.4 nm	[39]
AgNPs-L-Cys/Cit	5 ± 2 nm	[43]

When both systems were contaminated with 5ppm of Hg(II) ions showed an opposite behaviour, the LSPR band of AgNPs-3MPS system shifted from about 400 to 350 nm (blue solid line), whereas for the AgNPs-L-Cys/Cit from 400 to around 430 nm (red dashed curve). Measuring the effect of different Hg(II) concentrations with step of 1 ppm, we obtained a linear behaviour from 0 to 5 ppm and a limit of detection (LOD, 3σ) of 240 ppb for the AgNPs-3MPS system. Similarly, for the other silver nanoparticles system, we obtained a linear behaviour between 1 to 7.5 ppm and we estimated a LOD of 600 ppb. We tested the optical response of both systems in presence of several metal ions checking the shape and energy of the LSPR at the concentration of 5 ppm. For some of them we did not find any difference in the respective LSPRs, for some others we found a similar behaviour, namely a shift of the LSPR band to longer wavelengths (red shift). The optical behaviour of the surface plasmon resonance band for the two silver systems in presence of the different heavy metal ions at the concentration of 5 ppm is reported in Table 2. In the table, a positive value represents a red shift, while a negative value is referred to a blue shift. The AgNPs-3MPS system presented a low selectivity, showing a similar optical response towards Cd(II), Co(II), Cu(II), Mg(II) and Ni(II) (red shift), but evidencing in the case of Hg(II) an opposite behaviour with respect to the others contaminants (blue, more marked shift). Furthermore, the AgNPs-L-Cys/Cit was more selective with respect to the other system, since it responded with a red shift to Cr(III), Cu(II) and Hg(II) even if it is less sensitive. However, as already outlined, the opposite shift of the two systems in presence of mercury ions, makes this combined optical sensor really selective for that specific contaminant. A preliminary hypothesis about the different interaction mechanism for Hg(II) of the two systems, that can justify the opposite behaviour, is discussed in the next section.

A preliminary hypothesis of the opposite optical behaviour in presence of Hg(II)

Some preliminary considerations about the coverage level of the capping agents for the two AgNPs systems has to be done. The AgNPs-3MPS system has a capping agent amount that is about 10 times lower than the AgNO₃ content, which could mean the 3MPS molecules cover only partially the AgNPs surface. The low coverage level allows the Hg(II) ions to easily reach the NPs surface and to react with it, forming an amalgam with the external Ag atoms[44,45].

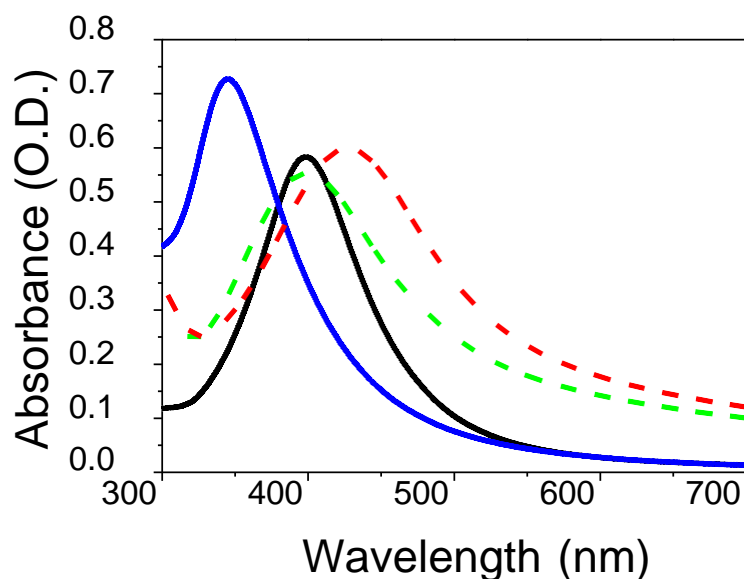


Fig. 2. UV-Vis absorption spectra of both AgNPs systems without and with 5ppm of Hg(II). AgNPs-3MPS as reference and with 5ppm of Hg(II) contamination are the solid black and the solid blue curve, respectively. AgNPs-L-Cys/Cit as reference and with 5ppm of Hg(II) contamination are the dashed green and the dashed red curve, respectively.

Table 2. heavy metal ions tested with both systems.

Metal ions at 5 ppm	Ag nano-system	
	NPs-3MPS	NPs-L-Cys/Cit
As(III)	\	\
As(V)	\	\
Ca(II)	\	\
Cd(II)	+ 11 nm	\
Co(II)	+ 17 nm	\
Cr(III)	\	+ 8 nm
Cu(II)	+ 6 nm	+ 6 nm
Fe(III)	\	\
Hg(II)	- 44 nm	+ 26 nm
K(I)	\	\
Mg(II)	+ 6 nm	\
Na(II)	\	\
Nd(III)	\	\
Ni(II)	+ 19 nm	\
Pb(II)	\	\
Zn(II)	\	\

The mechanism could be explained on the basis of the electrochemical differences of Ag(I) and Hg(II) ions. The standard reduction potential for Ag is +0.80V ($\text{Ag(I)} + \text{e}^- = \text{Ag(0)}$) whereas for Hg(II) it is +0.85V ($\text{Hg(II)} + 2\text{e}^- = \text{Hg(0)}$) and according to the electrochemical series, metals with a higher reduction potential act as better oxidising agents[46,47]. Therefore,

Hg(II) ions will reduce at the surface of AgNPs, while Ag atoms will oxidize, giving origin at the amalgam. This mechanism could explain the blue shift of LSPR band of AgNPs-3MPS.

In the other case, the two stabilizers (citrate and L-Cysteine) are about 14 times higher than the Ag(I) ions, thus the coverage of AgNPs surface is probably complete. The stability of AgNPs colloidal solutions is due to the electrostatic repulsions of functional groups of capping agents, indeed, L-Cys and Cit molecules with their carboxylate ($-\text{COO}^-$) groups prevent the aggregation of AgNPs in solution. When the AgNPs-L-Cys/Cit solution is in presence of Hg(II) ions, the latter cannot reach the bare surface of NPs. This favours the aggregation of the particles, and as consequence, we observe a red shift of the optical absorption and a broadening of the LSPR band.

Conclusions

In this study, we synthesized two different functionalized AgNPs in water, with a narrow size dispersion and a good stability over the time. We tested their optical response to several heavy metal ions monitoring the LSPR band before and after adding contaminated water. An opposite optical behaviour for the two systems in presence of Hg(II) ions have been measured. In the case of AgNPs-L- Cysteine/citrate, the plasmonic band shifted to higher wavelengths while in the case of AgNPS-3MPS shifted to lower wavelengths. This behaviour offers a very good selectivity in the detection of Hg(II) in water with a LOD of about 600 ppb. The opposite behaviour can be related to the different coverage level of NPs surface. For 3MPS Ag system, the capping agent amount is not enough to cover completely the NPs, thus the Hg(II) ions interact directly with the Ag external atoms, forming an amalgam which give rise to the blue shift in the absorption spectrum. For the other nano-system, where the coverage level is enough to completely shield the NPs surface, the Hg(II) ions interact with the particle surface, promoting the aggregation of AgNPs and as a consequence a red shift of the absorption spectrum was detected.

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