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# Hydrophilic silver nanoparticles for the treatment of water polluted by heavy metals

F. Bertelà<sup>1</sup>, A. Bellingeri<sup>2</sup>, L. Burratti<sup>1</sup>, P. Proposito<sup>3</sup>, M. L. Di Vona<sup>3</sup>, E. Sgreccia<sup>3</sup>, I. Corsi<sup>2</sup>, M. Marsotto<sup>1</sup>, G. Iucci<sup>1</sup>, C. Battocchio<sup>1</sup>, I. Venditti<sup>1\*</sup>

<sup>1</sup> Sciences Department, Roma Tre University, via della Vasca Navale 79, 00146 Rome (IT)

<sup>2</sup> Department of Physical, Earth and Environmental Sciences, University of Siena, Via Mattioli 4, Siena, 53100 (IT)

<sup>3</sup> Department of Industrial Engineering, University of Rome Tor Vergata, Via del Politecnico 1, Rome, 00133, (IT)

[iole.venditti@uniroma3.it](mailto:iole.venditti@uniroma3.it)

**Abstract.** Hydrophilic silver nanoparticles (AgNPs) are widely used in advanced biotechnologies, due to their versatile, easy, cheap preparations and due to their peculiar physico-chemical properties. It is well known that their surface functionalization plays a key role in defining the chemical-physical behaviour of AgNPs. If used for monitoring and remediation of heavy metals polluted water, the surface functionalization can direct the selectivity and sensitivity of the nanomaterial. Moreover, different capping agents can also induce different ecotoxicity. In this framework AgNPs are synthesised and properly functionalized using different capping agent, such as citrate (Cit), sodium 3 mercapto-1-propanesulphonate (3MPS), L-cysteine (Lcys) and glutathione (GSH). The opportune choice of these capping agents induces size control (in the range of  $\varnothing = 2\text{-}30$  nm) and make available selectively detection of heavy metal ions, such as Co(II), Hg (II) or Fe (III). These investigations confirmed that the multiple functionalized AgNPs are amazing and promising systems for monitoring and treatment of heavy metals polluted water.

## 1. Introduction

In the last decade, nanomaterials are showing how their peculiar chemical-physical properties can bring innovation and greater efficiency in the various application fields where they are used, such as in the fields of biotechnology, catalysis, optoelectronics and energy [1-9].

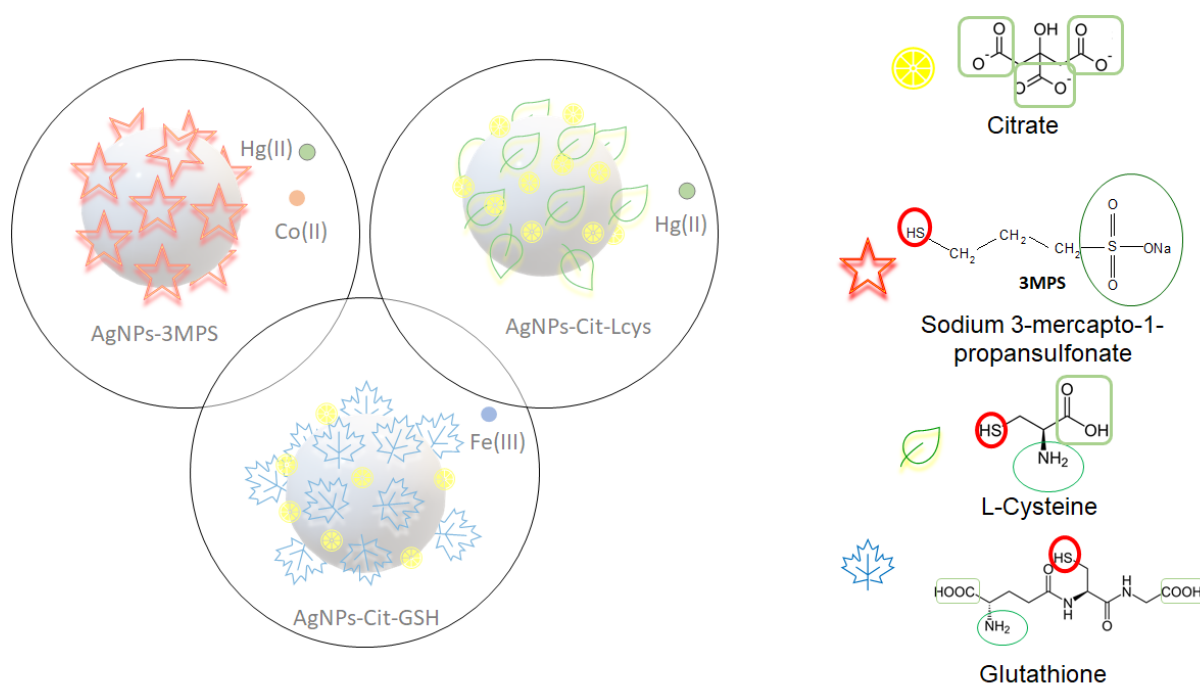
Among others, the silver nanoparticles (AgNPs) are widely used in advanced biotechnologies, due to their physico-chemical properties and versatile, easy and cheap preparations [10-12]. It is well known that their surface functionalization plays a key role in defining the chemical-physical behaviour of AgNPs [13-15]. In fact, the choice of a specific capping agent affects the hydrophilic or hydrophobic character of the nanomaterial, as well as its ability to self-assemble or aggregate. Furthermore, the presence of specific functional groups can facilitate the interaction with other species present in the vicinity of the particles, thus making them sensitive and selective for these species. When used for monitoring and remediation of heavy metal polluted waters, surface functionalization can address the selectivity and sensitivity in pollutant capture [16-21].

On the other hand, different capping agents can also induce different ecotoxicity just because of the different surface chemistry. This aspect is extensively studied and reported in recent literature. Lekamge



*et al.* [22] for example, in a recent work, present of differently functionalized AgNPs, highlighting how, the effect of the stabilizing molecule present on the surface must be considered, as also reported by other authors [23-28]. Hence the need for a synthetic approach that is based on green chemistry but also and above all an initial step based on the concept of “safe by design”: designing the material for the desired application, also considering its low ecotoxicity among the desired requirements [29-34].

In this work we compare the behavior as heavy metal sensors of silver particles with three different surface functionalizations: sulfonate (3MPS), citrate (Cit) and L-cysteine (Lcys), or citrate and glutathione (GSH), as schematized in Figure 1. The first two systems have already been studied by our group and showed optical response for Co(II) and Hg(II) in the case of AgNPs-3MPS, while the plasmon band of AgNPs-Cit-Lcys changes in presence of mercury [17,28,35]. AgNPs-Cit-GSH particles are newly synthesized and are selective and sensitive only to Fe(III) ions. The opportune choice of these capping agents induces size control (in the range of  $\varnothing = 5-30$  nm), brings different selectively detection of heavy metal ions. It is therefore evident that, with the same synthetic method, range of dimensions and silver cores, the role of surface functionalization plays key and determining role regarding the selectivity of these nanomaterials used as sensors and/or absorbers of heavy metals in polluted waters.



**Figure 1.** Different selectivity of silver nanoparticles, as optical sensors for heavy metals ions such as Co(II), Hg(II) and Fe(III), according to their surface functionalization.

## 2. Materials and methods

### 2.1. Materials

Reagents and solvents of analytical grade were purchased from Sigma-Aldrich (St. Louis, MO) and were used without further purification. Silver nitrate ( $\text{AgNO}_3$ , 99.9% pure), trisodium citrate (Cit, 99% pure), sodium 3-mercaptopropionate (3MPS, 98% pure) L-Cysteine (L-cys, 99% pure), L-Glutathione reduced (GSH, 98% pure), sodium borohydride ( $\text{NaBH}_4$ , 99.9% pure). Metal ions contamination was accomplished by using the following salts:  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . For all the solutions, we used deionized water (electrical conductivity less than  $1 \mu\Omega/\text{cm}$  at room temperature) obtained from Millipore Milli-Q water purification system.

## 2.2 Instruments

UV-Vis spectra were run in H<sub>2</sub>O solution by using quartz cells with a Shimadzu 2401 PC UV-vis spectrophotometer and single-use UV-PMMA cuvettes with Perkin-Elmer Lambda 750 UV-Vis-NIR for sensing test characterization.

Size distribution of AgNPs (50 mg/L) have been investigated by means of Dynamic Light Scattering (DLS, Malvern instruments), combined with the Zetasizer Nano Series software (version 7.02, Particular Sciences) at T = 25.0 ± 0.2 °C in milliQ water. Correlation data have been acquired and fitted in analogy to our previous work [36].

## 2.3 AgNPs synthesis

The AgNPs stabilized with 3MPS or Lcys were prepared and characterized in analogy to literature reports [25,28]. Main characterizations for AgNPs-3MPS: UV-Vis ( $\lambda_{\max}$  [nm], H<sub>2</sub>O) = 400 nm;  $\langle 2R_H \rangle$  ([nm], H<sub>2</sub>O) = 8 ± 3; Z- potential = -44 ± 5 mV; main characterizations for AgNPs-Cit-Lcys: UV-Vis ( $\lambda_{\max}$  [nm], H<sub>2</sub>O) = 400 nm;  $\langle 2R_H \rangle$  ([nm], H<sub>2</sub>O) = 8 ± 1 nm. For the AgNPs stabilized with Cit and GSH different experimental condition were performed as showed in table 1. The best sample was sample E, in which 1 mL of GSH solution (0.002 M), 50 mL of Cit solution (0.01 M) and 5 mL of AgNO<sub>3</sub> solution (0.05 M) were added sequentially in a flask, provided with a magnetic stir. After 10 minutes of degassing with Argon, 4 mL of NaBH<sub>4</sub> solution (0.016 g in 4 mL distilled water) were added. The mixture was allowed to react at room temperature for 2 h and then the suspension was purified by centrifugation (13,000 rpm, 10 min, 2 times with deionized water). Main characterizations for AgNPs-Cit-GSH: UV-Vis ( $\lambda_{\max}$  [nm], H<sub>2</sub>O) = 380 nm;  $\langle 2R_H \rangle$  ([nm], H<sub>2</sub>O) = 30 ± 5; Z- potential = -44 ± 2 mV

**Table 1.** Experimental conditions for AgNPs-Cit-GSH synthesis.

ID	GSH (0.002M) mL	Cit (0.01M) mL	AgNO <sub>3</sub> (0.05M) mL
A	5	10	5
B	2.5	10	5
C	1	10	5
D	1	30	5
E	1	50	5

## 2.4 Sensing tests

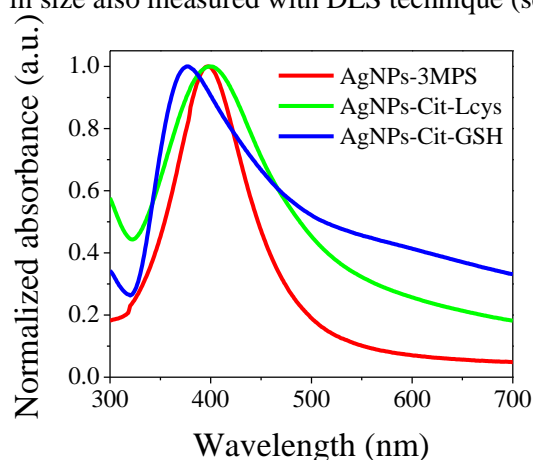
A fixed volume of AgNPs in water was mixed with a fixed volume of water solution containing the heavy metal ions at specific concentration (5ppm). After five minutes of interaction of the nanoparticles with the metal ions, the optical absorption spectra were collected in order to verify possible changes (shape, energy and intensity) of the typical localized surface plasmon resonance (LSPR).

## 3. Results and discussions

### 3.1 AgNPs synthesis and characterizations

The syntheses of the nanoparticles are carried out by reduction in the aqueous phase using sodium boron hydride [25,28,37,38]. By using different capping agents, in suitable quantities to obtain stable particles in water, different particle sizes are also obtained, smaller and larger than 10 nm. Indeed, for AgNPs-3MPS, AgNPs-Cit-Lcys and for AgNPs-cit-GSH the dimensions in aqueous solution are respectively  $\langle R_H \rangle = 8 \pm 3$  nm,  $8 \pm 1$  nm and  $30 \pm 5$  nm. On the other hand, the Z potential remains optimal, confirming the stability of the particles in water, with values around -40 mV [25,28]. Moreover, the presence in the synthesis mixture of different stabilizers (3MPS, Cit and Lcys or GSH) allows to insert different functionalities on the surface: the thiol sulfurs establish strong covalent bonds with the silver surface

and even the oxygens are able to interact and stabilize the particle. In addition, various functionalities remain (amino or acid or sulphonate) facing outwards and available for interactions with the chemical surroundings. The possibility of synthesizing the different functionalities allows to obtain high selectivity of these systems towards different heavy metal ions, in particular the AgNPs-3MPS towards Co(II) and Hg(II), the AgNPs-Cit-Lcys towards Hg(II) and AgNPs-Cit-GSH towards only Fe(III), as schematized in Figure 1. Naturally, for the three types of silver nanoparticles, the surface plasmon resonance phenomenon occurs, with the typical peak in the viable area ranging from 380 to 400 nm in water, depending on the size and capping agent. Figure 2 shows the normalized UV-Vis spectra of the three types of silver nanoparticles in aqueous solution. The particles capped with 3MPS and AgNPs-Cit-Lcys show a symmetric LSPR band peaked at 400 nm, while the AgNPs-Cit-GSH has an asymmetric absorption band centred at 380 nm, in addition a wide and intense scattering from 500 to 700 nm underlines the polydispersity in size also measured with DLS technique (see below).



**Figure 2.** Normalized Uv-vis spectra of AgNPs-3MPS (red line) AgNPs-Cit-Lcys (green line) and AgNPs-Cit-GSH (blue line, sample E).

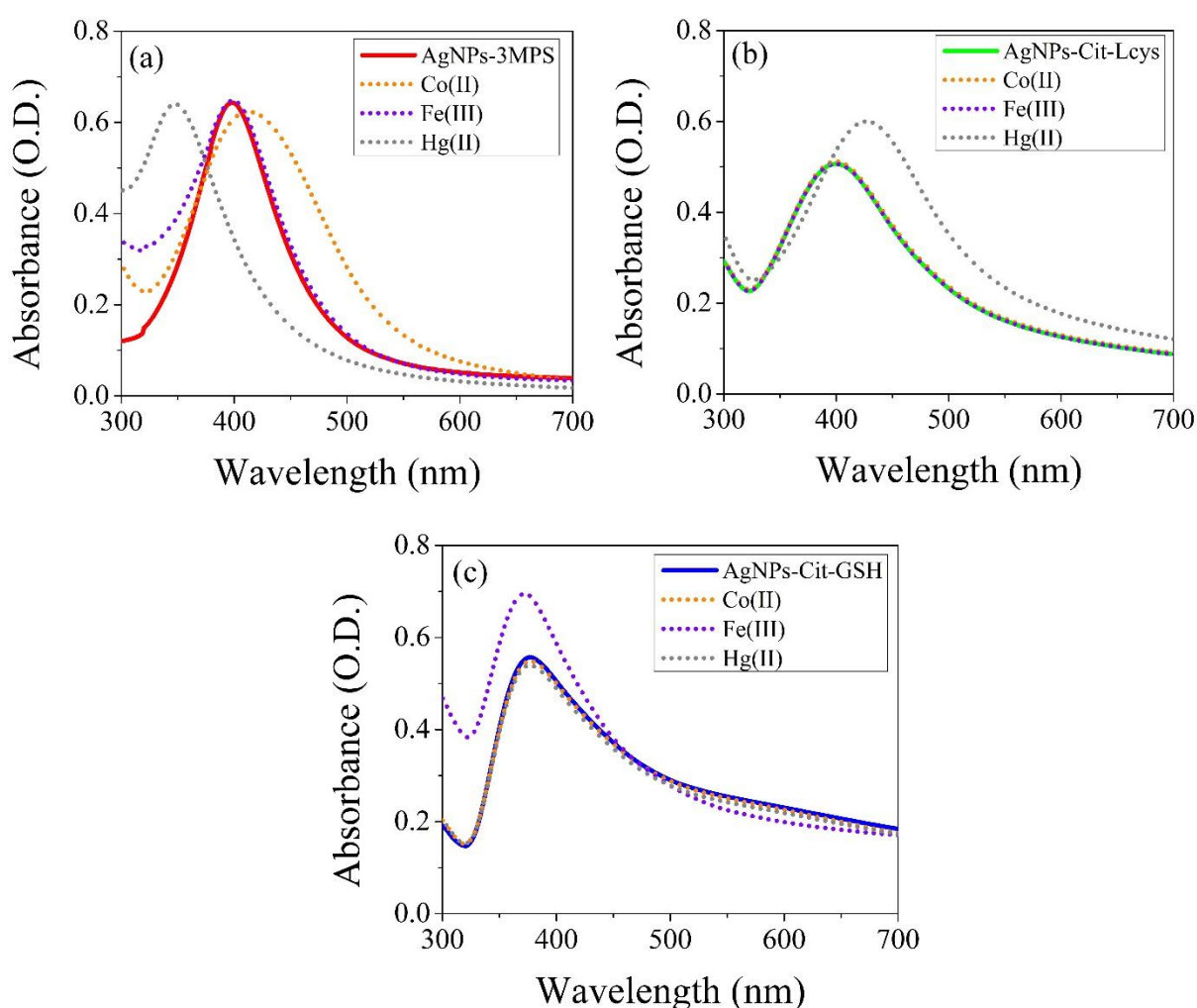
DLS studies were also conducted on the new synthesized nanoparticles with glutathione, to verify their behavior and stability in solution. The hydrodynamic diameter ( $\langle 2R_H \rangle$ ) measurements confirmed what was suggested by the UV-vis spectroscopy data. Samples A, B, C are extremely polydisperse and aggregated, so much so that the samples did not return any measurements. For sample D, on the other hand, a better situation is observed, even if there is a certain degree of polydispersity and the presence of aggregates. Finally, for sample E the average of hydrodynamic diameter is  $\langle 2R_H \rangle = 30 \pm 5$  nm and measuring a potential Z equal to  $-44 \pm 2$  mV.

**Table 2.** DLS data for AgNPs-Cit-GSH: average of hydrodynamic diameter ( $\langle 2R_H \rangle$ ), polydispersity index (PI) and Z-potential.

ID	$\langle 2R_H \rangle$ (nm)	PI	Z potential (mV)
A	1000	-	$-14 \pm 1$
B	-	-	-
C	>1000	-	$-13 \pm 1$
D	$200 \pm 50$	0.6	$-38 \pm 1$
E	$30 \pm 5$	0.4	$-44 \pm 2$

### 3.2 Sensing tests

Among the inorganic components that may be present in water, some are toxic and in particular those commonly known as "heavy metals": cadmium, chromium, lead, arsenic, mercury, nickel, cobalt, iron. Silver nanoparticles are known for their ability to act as optical sensors of these pollutants [39]. In Figure 3, the plasmon absorption peaks belonging to AgNPs-3MPS (a), AgNPs-Cit-Lcys (b) and AgNPs-Cit-GSH (c), respectively. The effect on the SPR band in presence of 5 ppm of Co(II), Fe(III) and Hg(II) is also presented in the Figure 3. In the case of 3MPS-capped silver nanoparticles, cobalt ions produce a slight redshift (15 nm) and a broadening of the plasmon band, because of interaction among Co(II) ions and sulfonic groups of the 3MPS [17]. An opposite behavior in presence of Hg(II) ions occurs, indeed the SPR peak shift towards shorter wavelengths ( $\Delta\lambda = 50$  nm), the interaction mechanism is due mainly to the amalgam formation between Ag metal core and Hg [27]. The Fe(III) ions have no effect on the silver nanoparticles band.



**Figure 3.** UV-Vis spectroscopy of the three different AgNPs systems: (a) AgNPs-3MPS (red solid line), (b) AgNPs-Cit-Lcys (green solid line), (c) AgNPs-Cit-GSH (blue solid line) in presence of 5 ppm of Co(II) (orange dotted line), Fe(III) (violet dotted line) and Hg(II) (grey dotted line).

In the case of AgNPs-Cis-Lcys, Co(II) and Fe(III) do not affect the SPR band, while Hg(II) ions produce a 30 nm of redshift, due to the direct interaction with metal surface [19]. In the last case (AgNPs-Cit-GSH), only the Fe(III) produces a change in the SPR band. Further analyzes are needed to shed light on the interaction mechanism between Fe(III) ions and AgNPs-Cit-GSH.

#### 4. Conclusions

Silver nanoparticles, due to the rapid development of technologies for their versatile chemical synthesis and their characteristics such as stability, size modulation, functional flexibility and low cost, represent promising new optical sensing materials for water pollutants. Among others, the systems reported here, functionalized with different stabilizers, have allowed to obtain selective optical sensors for Co(II), Hg(II) and Fe(III), present in water at 5 ppm. These results highlight how these systems are versatile and promising for detection and treatment of waters polluted by heavy metals.

**Author Contributions:** Conceptualization, I.V., P.P, I.C. and C.B.; methodology F.B., A.B. and I.V. designed and performed the AgNPs synthesis and UV–Vis measurements and evaluations. L.B. and P.P. performed the sensing tests. FT-IR measurements and the data analysis were performed by M.M., G.I. and C.B.; A.B. and I.C. performed DLS and TEM studies and the data analysis. All authors contributed to the paper writing and revision. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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