

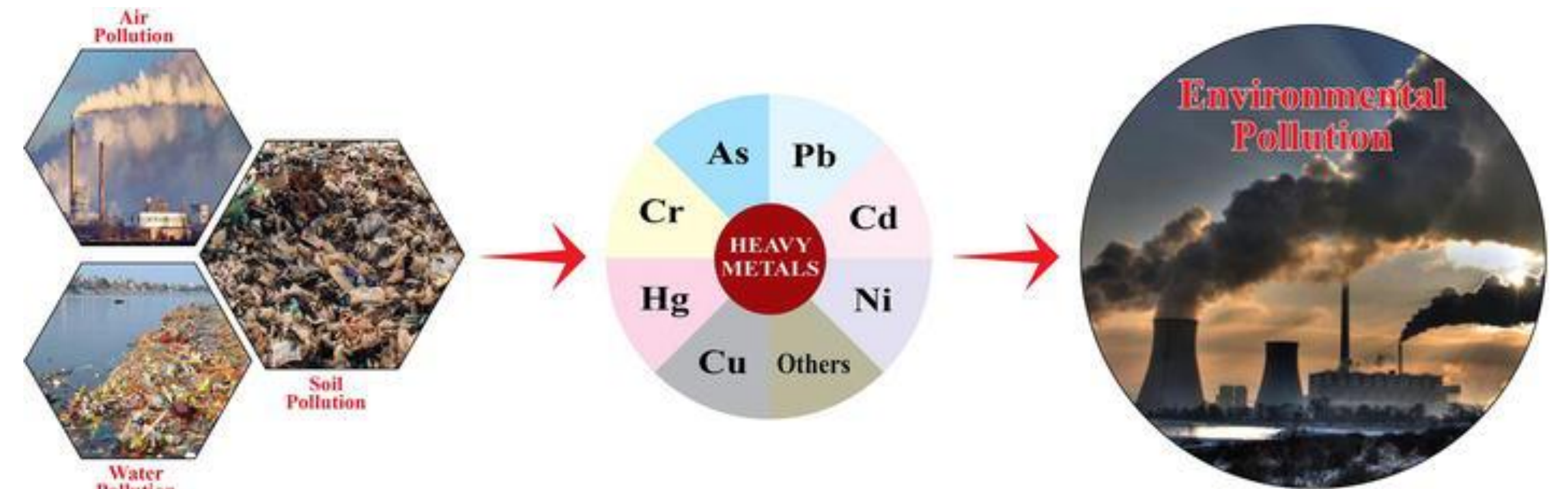
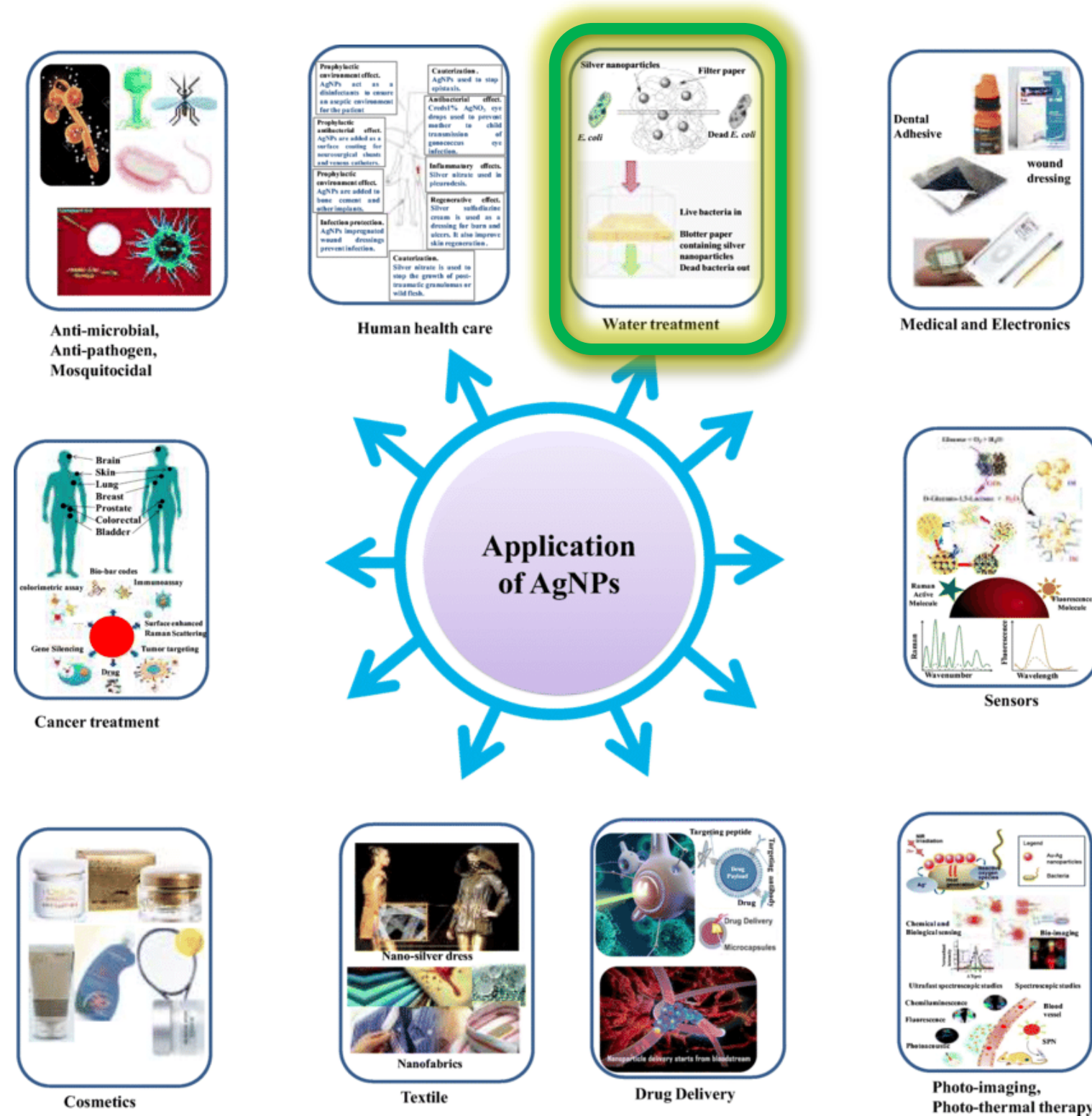
# Hydrophilic silver nanoparticles for the treatment of water polluted by heavy metals

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Silver nanoparticles (AgNRs) are being applied as optical sensing materials and antimicrobial agent in many biotechnological applications. Their wide success is due to their unique chemical and physical properties, and well-established and versatile strategies for surface modification.[1,2]



Natural activities (e.g. geological weathering, precipitation, wave erosion, wind and bioturbation) and anthropogenic activities (e.g. rapid industrialization, urbanization, agricultural runoff and transport) play a key role in the spread of heavy metals (HM) in habitats marine of aquatic ecosystems such as rivers and estuaries. Water contamination by HMs is a critical environmental problem that negatively affects plants, animals and human health. Even at very low levels, heavy metals are highly harmful to marine species. Due to environmental persistence, bioaccumulation and biomagnification of food chains and the toxicity of these elements, contamination of water bodies with heavy metals is a global problem. AgNPs and their composite systems are excellent tools both for the detection and for the absorption and removal of HM from water.

**GOAL:** Synthesis of functionalized AgNPs with the aim to obtain strongly hydrophilic nanomaterials, suitable for sensing applications in water. AgNPs were synthesized by wet reduction, and they were investigated by means of UV-Visible Spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR) and Synchrotron Radiation induced X-ray Photoelectron Spectroscopy (SR-XPS). Moreover, Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) observations confirmed the nanosize.

AgNPs $R_H$ (nm)	Capping agent	Selective for	LOD (ppm)	Acute toxicity*
$5 \pm 3$	3MPS	Ni (II), Co(II)	0,5	yes
$9 \pm 4$	Cit-Lcys	Hg (II)	1	no
$8 \pm 4$	Cit-GSH	As(III)	Under investigation	Under investigation

\* Details ecotoxicity on microalgae (1–1000 µg/L) and microcrustaceans (0.001–100 mg/L), from the freshwater and marine environment, are reported in our recent papers [4,5]

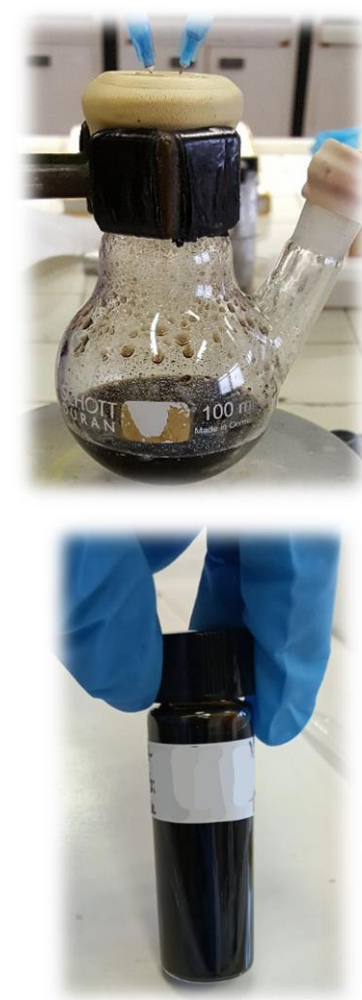
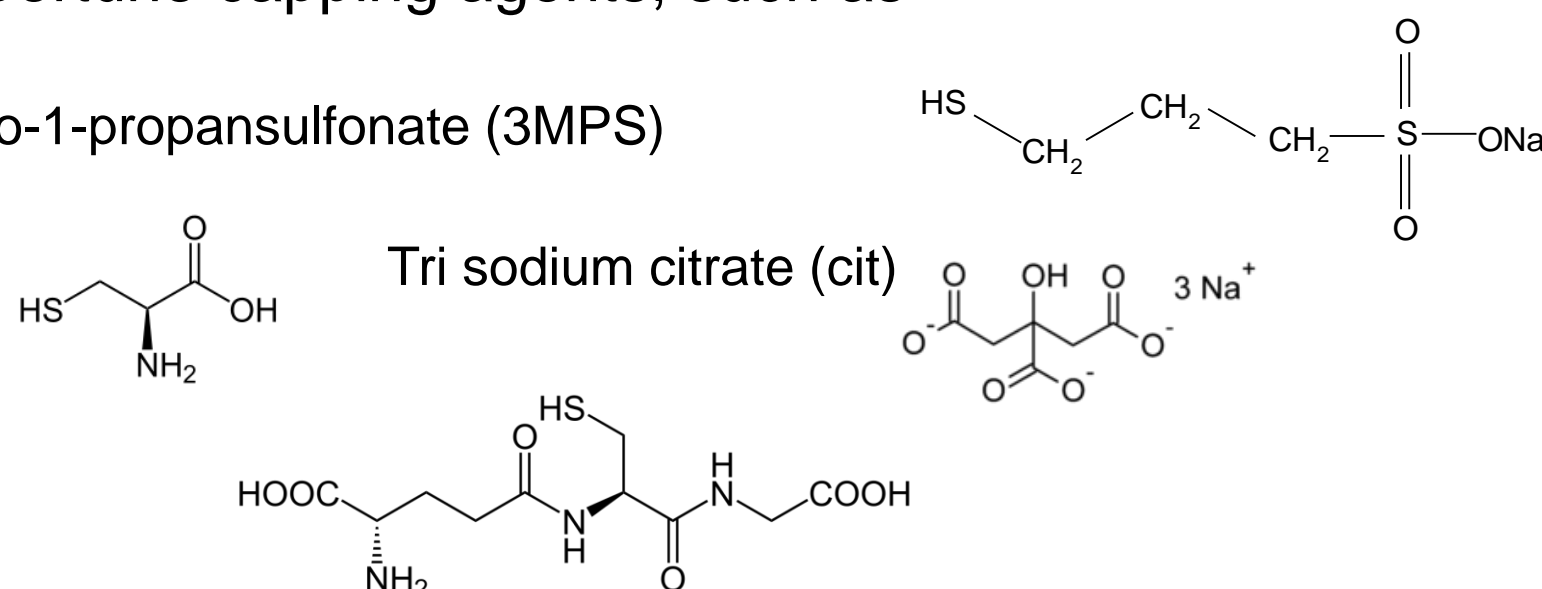
## AgNPs: Synthesis and Functionalization

Synthesis is wet reduction of  $AgNO_3$  by sodium borohydride in presence of opportune capping agents, such as

Sodium 3-mercaptopropionate (3MPS)

L-cysteine (L-cys)

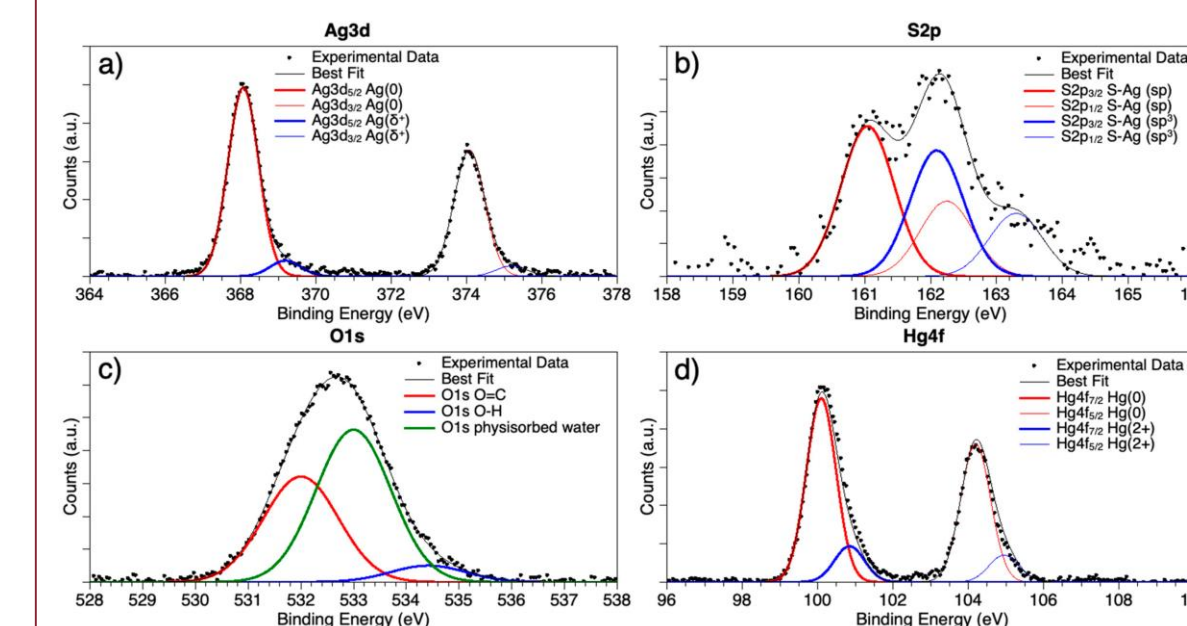
Glutathione (GSH)



AgNPs show a peak of plasmonic absorption at about 400 nm. When suitably functionalized particles interact with metal ions, aggregation phenomena can occur which lead to a red shift of the plasmon. This makes AgNPs excellent optical sensors. In fact, different hydrophilic capping agents induce different selectivity to metal ions in water and different ecotoxicity.[3-5]

## SR-XPS Investigations

SR-XPS analysis carried out at C1s, N1s, S2p, Ag3d core levels confirmed the NPs chemical composition and allowed to assess the capping agent molecular stability. Moreover, after the interaction with metal ions in water, the relationship between NPs and metal ions were addressed [3,4]. In particular here the SR-XPS data about AgNPs-cit-Lcys and Hg(II) interaction [4].

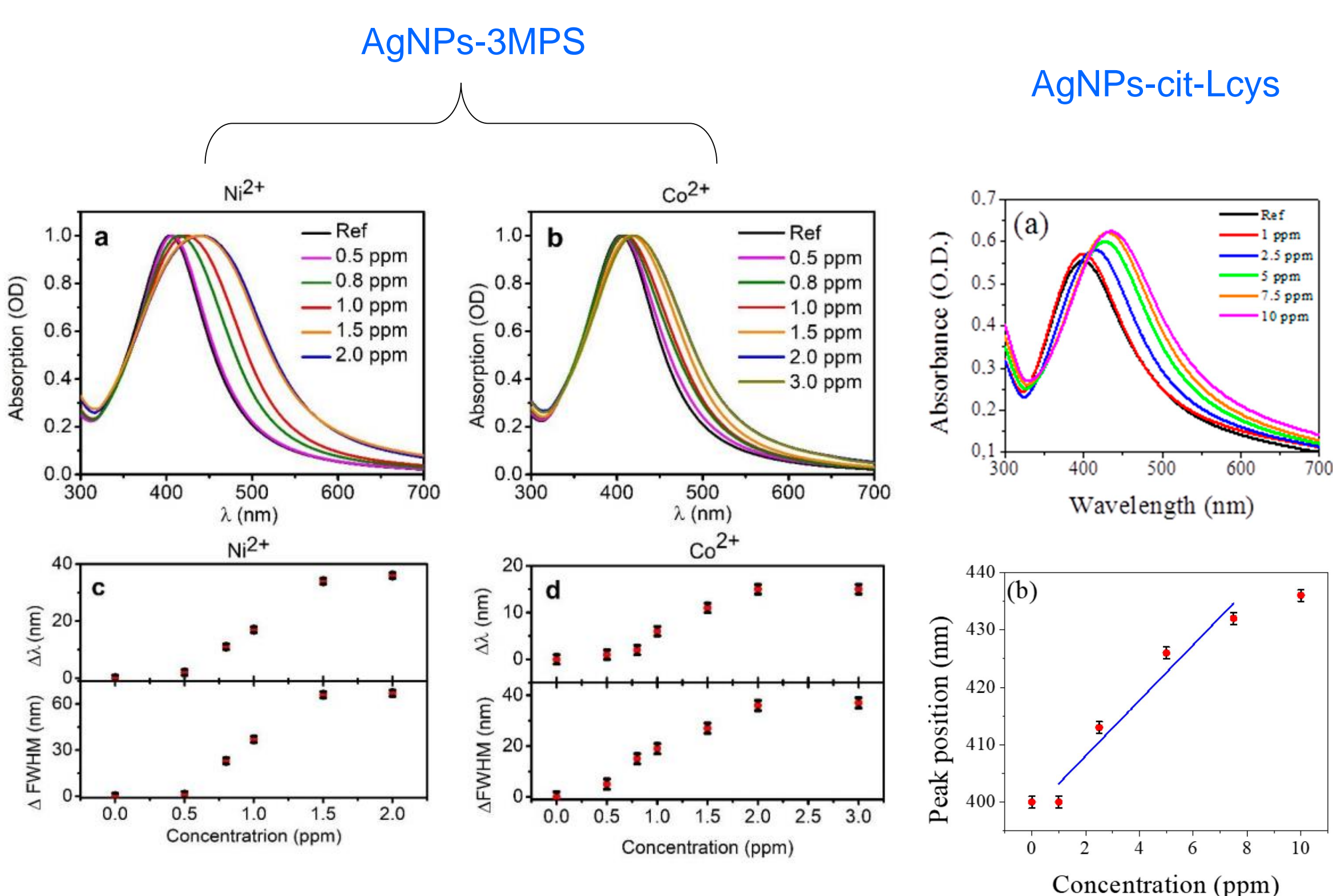
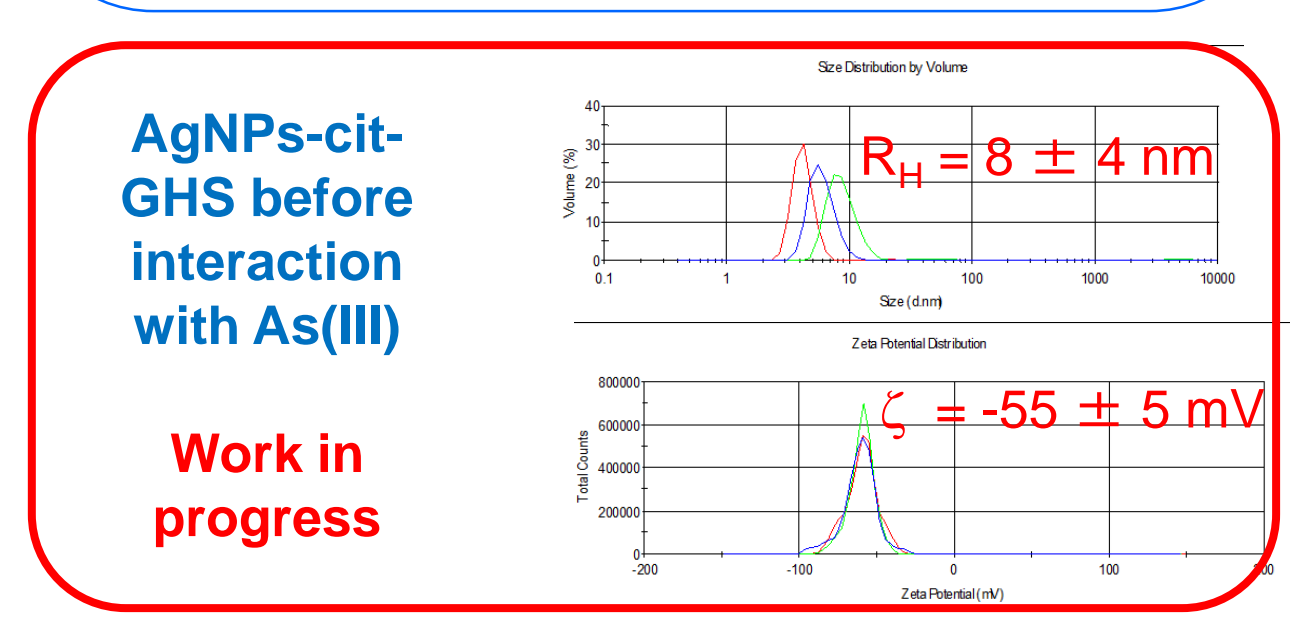
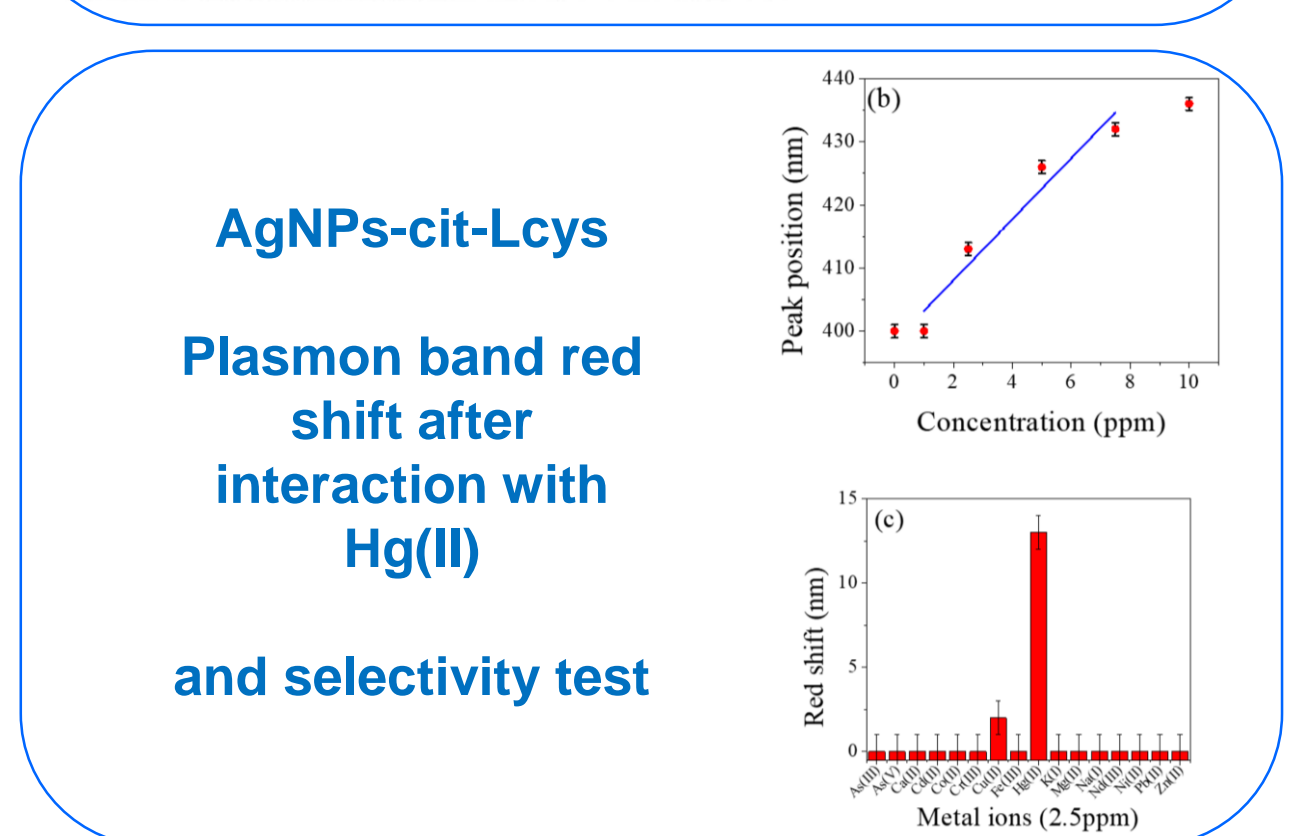
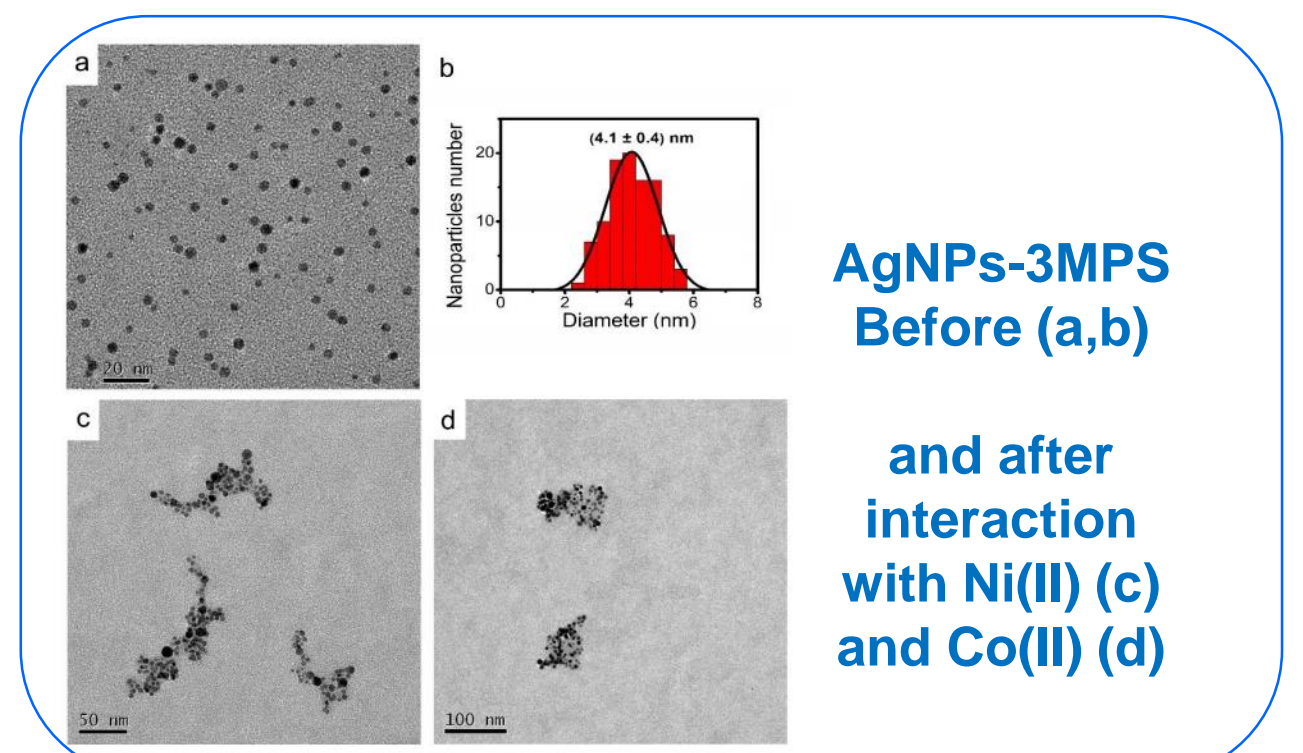


SR-XPS spectra collected on AgNPs-cit-Lcys +  $Hg^{2+}$  aggregates at (a) Ag3d; (b) S2p; (c) O1s and (d) Hg4f core levels

Ag3d spectra are asymmetric at high BE, indicating the spin-orbit pair at lower BE values ( $Ag3d_{5/2} = 368.08$  eV) associated with metallic silver at the NPs core, and the signal at higher BE, due to positively charged silver atoms at the surface, interacting with the capping agents. The S2p spectra are composite, showing two spin orbit pairs with similar intensity, both indicative for sulphur atoms covalently bonded to silver, but with two different hybridizations: the spin-orbit pair at lower BE ( $S2p_{3/2} = 161.05$  eV) is indicative for S-Ag bonds with sp hybridized sulphur; the signal at higher BE ( $S2p_{3/2} = 162.09$  eV) suggests S-Ag bonds with sp<sup>3</sup> S atoms. This suggests that L-cys molecules preferentially tend to directly bond the Ag surface, inducing the most part of Cit molecules to form a shell around the first L-cys layer, in a "layer-by-layer"-like arrangement. Moreover, the occurrence of a signal indicative for metallic Hg is in excellent agreement with literature, where a direct interaction between Hg and Ag atoms at the nanoparticle surface was envisaged.

## UV-VIS, TEM and DLS studies

UV-visible spectroscopy, Transmission electron microscopy (TEM) and Dynamic Light Scattering (DLS) in water confirm the nanosize and the low polydispersity of AgNPs. Furthermore, after metal ions interaction the aggregations phenomena are verified.



## CONCLUSIONS

Hydrophilic AgNPs were synthesized and functionalized with different capping agents. Opportune functionalization allow specific selectivity for metal ions detection in water. TEM and DLS studies confirmed the nanosizes (5-10 nm) and the aggregation phenomena in presence of metal ions pollutants. Furthermore, the SR-XPS investigations made it possible to examine the chemical structure and the interaction between capping agents and metal ions. These results show that highly hydrophilic AgNPs are amazing and versatile optical sensor materials, optimal tools for water protection.

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### References:

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