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TUNNING GOLD NANOPARTICLES SIZE AND SURFACE CHARGE BY OIL-IN-WATER MICROEMULSION TEMPLATE

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The aim of this paper was to present a versatile method of spherical gold nanoparticles synthesis using oil-in-water microemulsiontemplate in which the reduction of Au^{3+} ions to Au^{o} was obtained by physical UVphotoreductionas a clean, cost-effective and convenient synthesis methods. Since the simple gold nanoparticles undergo agglomeration due to Van der Waals forces and high surface energy,by adding two tiolsligands, such as cysteaminemonoclorhidrate and 3-sulphonate mercaptopropan sodium stable nanoparticles with pozitively and negatively surface charges have been obtained. The size, shape, stability, structure and surface charge of AuNP have been confirmed by DLS (size and Zeta Potental)measurements, UV-Vis spectroscopy, XRD and EDXRF analysis and HRTEM micrographs.

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Keywords: O/W microemulsion, Photoreduction, gold nanoparticles, Thiols, Stability, Surface charge

1. Introduction

Over the past few decades, metallic nanoparticles have gained incresed interest due to their unique phsysical and chemical properties different from those of the bulk states or atoms, such as quantum size effect and specific electronic structures [1-5].As a result of these specific features the potential applications have grown rapidly, metallic nanoparticles being used in many fields, such as catalysis, optics, biochemistry, medicine, pharmacy, energy and life science [6-10]. Especially, noble metallic nanoparticles, such as gold nanoparticles (AuNP) with their associated strong plasmon band are probably the most remarkable members of the metal nanoparticle group [11, 12].

"Top down" and "bottom up"approach have been developed in order to synthesize AuNP. The "top down"method involves breaking down the bulk state Au material and is a limited procedure concerning the control of size and shape of AuNP as well as further functionalization [13]. In contrast, in the "bottom up"strategy, the AuNPoriginate from individual molecules when the reduction of gold precursor solution may be physical, chemical or biological.Clasical procedure for AuNP synthesis is based on the chemical reduction of tetracloroauric acid with sodium citrate (Turkevich method) [14]and requires high temperature (60^{o}C).Biological reduction is considered a green aproach and leads to stable AuNP, but they are not uniform and are synthesized fairly slowly [15]. A more clean, cost-effective and convenient method is physical photoreduction of AuNP[16-18].

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Recently, the authors developed a novel and straight forward approach for the synthesis of AuNP in W/O microemulsion template, in which the reduction of Au^{3+} to Au^{o} take place under UV irradiation and keep the features of template[19]. The use of microemulsion template is one of the most advantageous ways to synthesize AuNP in a “bottom up”approach. Microemulsions arethermodinamically stable and clear colloidal dispersion comprised of oil, water and surfactant. Different structure can be formed as such: water-in-oil (W/O) or oil-in-water (O/W) droplets, and bicontinue structure, over a wide range of composition depending of the properties of the surfactant and the oil. An oil-in-water microemulsion is similar to a direct micelle while the water-in-oil microemulsion is toppologicalanalogous to a reverse micelle [20, 21].

The W/O microemulsion method offers a lot of advantages with respect to others (co-precipitation in solution, sol-gel, flame-spray pyrolysis, laser evaporation, high energy milling), namely, the use of a simple equipment, homogeneous mixing, high degree of particles size and composition control, formation of AuNP with high surface area and the used of soft condition of synthesis near ambient temperature and pressure [22]. The first application of W/O microemulsion for noble metal nanoparticles synthesis was reported in 1982 [23]. The main strategy for the AuNP synthesis in W/O microemulsion consists in mixing two microemulsions, one containing the gold precursor solution and the other one containing the reductionagend (usually $NaBH_4$) [24].Upon mixing procedure, both reactants (gold precursor solution and reduction agent) will contact each other due to the coalescence and droplet collisions and will react to form AuNP which remaine confined to the interior of microemulsion droplets.Even through AuNP obtained by W/O microemulsion shows superior properties and performance, at the industrial level this method has no good acceptance, mainly due to the large amount of solvents (oils) which represent the main component of these systems being the continuous phase [25].

From environmental and applied point of view, the posibility of preparing metal nanoparticles using O/W microemulsion template has several advantages over W/O microemulsion since the major continuous phase is water: the ratio of water and oil phase is far grater than 1, the consumption of organic matter is less and the cost is relatively low. The main applications of O/W microemulsion were preparation of lipidic and polymeric nanoparticles [26, 27] and in pharmaceuticals and detergent formulations [28, 29]. O/W microemulsion started to be used for the synthesis of inorganic nanoparticles only until recently hence, the literature is not abundant with this subject. Li et al. [30] reported the O/W microemulsion for the synthesis of various inorganic nanoperticles, such as metallic nanoparticles (Ag, Cu), semiconductors (Ag_2S, PbS, CdS, ZnS, CdSe, PbSe, Ag_2Se), fluorides (CaF_2, YF_3, NdF_3, PrF_3), phosphates ($CePO_4$ and $HoPO_4$) and chromates ($BaCrO_4$ and $PbCrO_4$), and all the products were made up of small particles with average size ranging from 2 to 13 nm.

To the best of our knowledge there is no study regarding the synthesis of AuNP in O/W microemulsion template. Moreover, in this study one proposed the synthesis of AuNP by the Au^{3+} to Au^{o} reduction under UV irradiation in O/W microemulsiontemplate,as a clean, cost effective and convenient method for synthesis of spherical and stable AuNP. Since simple AuNPare very active and prone to coagulate due to the Van der Waals forces and high surface energy, ligands are necessary for stabilization. With this aim in mind two ligands from thiols class, cysteaminemonoclorhidrat (CS) and sodium 3-sulphonate mercaptopropan (MS), were used in order to maintain the AuNP size as the initial oil droplets size dispersed in continuous water phase. The Dinamic Light Scattering (DLS), UV-Vis spectroscopy, TEM microscopy, XRD and EDX analysis were used to confirm the size, shape, structure and stability of thiol – AuNP obtained.

2. Materials and methods

2.1. Materials

Hydrogen tetrachloroaurate (HAuCl4), Polyoethylene glycol tert-octylphenyl ether (Triton X-114), n-heptan, butanol, cysteaminemonoclorhidrahte and 3-sulphonate mercaptopropan sodium were provided by SIGMA-ALDRICH. All reagents were analytical grade and were used without further purification. Also ultrapure Millipore water was used for the preparation of the microemulsion sample.

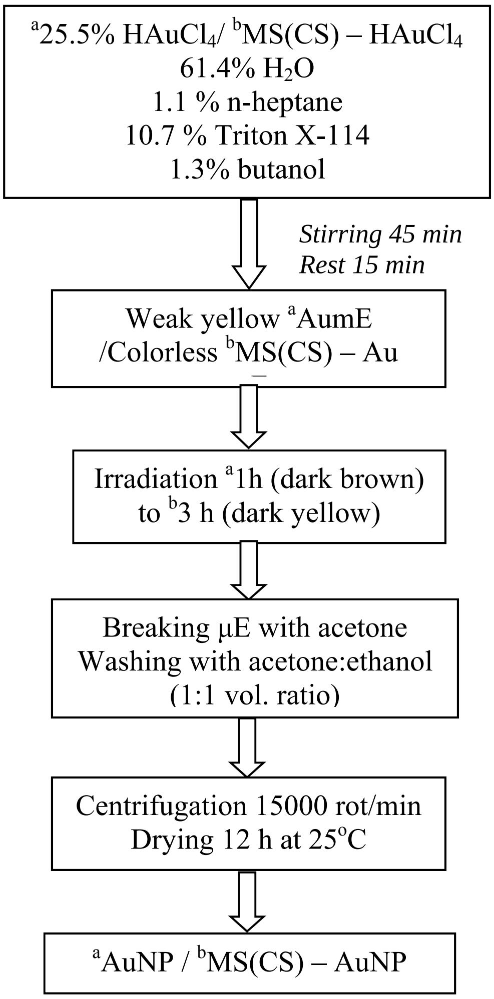
2.2. Methods

2.2.1. Synthesis of simple and thiol – AuNP

The AuNP were synthesized using a technique in which physical irradiation procedure (λ = 254 nm) undergoes in O/W microemulsionas soft chemical route. AuNP synthesis involves several steps as one can see in Scheme 1. Initial O/W microemulsionconsisted in water-$HAuCl_4$/n-heptane/Triton X-114/butanol quaternary system were stirred over 45 minutes and irradiated during 1 hin a Luzchemphotoreactor, LZC-4X equipped with eight lamps, each of 12 W, the intensity per each lamp used were 0.3 mV/cm^2. Constant stirring of the microemulsion was ensured by using a magnetic stirrer and the temperature was kept constant throughout the reaction time by the ventilation system in the main chamber of the photoreactor. After 1 h of irradiation the O/W microemulsion containing AuNP dispersed inside was converted from a weak yellowmicroemulsion to a dark brown one.

By using the same procedure AuNP stabilized with thiols molecules have been prepared, in this case the O/W microemulsion being irradiated during 3 h. Thiol – AuNP synthesis involves preparation of an initial solution of $HAuCl_4$ and MS/CS 10^{-1}M. After 1 and even 3 h of irradiation the microemulsion containing thiol – AuNP turns from colorless to dark-yellow indicating that amicroemulsion with specific size is obaied.

In order to obtain thiols – AuNP as powders the O/W microemulsion was broken by addition of asolution containing acetone:ethanol, 1:1 volumetric ratio. The resulting nanoparticles were washed alternatively five times with acetone and etanolto remove the excess of surfactant, oil and thiols compounds and allowed to dry at ambient temperature for 12 h.



Scheme 1. Schematic diagram preparation of simple AuNP (^{a}) and thiol – AuNP (^{b})

2.2.2. Characterization technique

2.2.2.1. DLSand Zeta Potential measurements

The size and Zeta Potential measurements were performed on a Malvern Nanosizer Equipment (NANO-SZ). The sizes of simple and thiol – AuNP in the pristine microemulsion were registered based on Dinamic Light Scattering (DLS) principle, at 90^o scattered light. The electrophoretic mobility was converted into Zeta Potential by using the Helmholtz–Smoluchowski equation. All the measurements were done in triplicate at 25^oC constant temperature.

2.2.2.2. UV-Vis spectroscopy

The spectral characterization of AuNP and thiol – AuNP dispersed in pristine microemulsion was evaluated using a Jasco V-570 spectrophotometer.

2.2.2.3. XRD analysis

The X-Ray Diffraction (XRD) measurements were performed on a RigakuUltima IV (CuK_α radiation) eqquiped with parallel optics.

For qualitative analysis, the X-Ray diffractogram were acquired in Bragg-Brentano geometry, in $25^o – 112^o$ 2θ interval, with 0.5^o step and 2 seconds time step measurement.

2.2.2.4. EDXRF analysis

Compositional analyses were carried out using an Electron Dispersive X-Ray Fluorescence (EDXRF) spectrophotometer, SPECTRO MIDEX M model with the following configuration: 30 W-Mo radiations X tube and SDD detector with 160 eV resolutions on Mn-Kα line.

The conditions of the EDXRF analysis were:

1. He purging direct excitation, 1 mm slot, operating voltage U = 44.70 kV, current intensity I = 0.30 mA, measurement time per aquisition 180 s, number of energy channel used 2048;
2. He purging direct excitation, 2 mm slot, operating voltage U = 18.87 kV, current intensity I = 0.30 mA, measurement time per aquisition 300 s, number of energy channel used 1024

2.2.2.5. HR-TEM analysis

The size of dried AuNP was evaluated using High-Resolution Transmission Electron Microscopy (HR-TEM) on a Tecnai G2F30 S-TWIN model. Also, the Selected Area Electron Diffraction (SAED) on this model was performed in order to identify the crystal structure and to examine the crystal defects.

3. Results and discussion

Since the application of AuNP simple or functionalized with ligands has undergone significant growth in the past few years, the development of various techniques for the synthesis requires using clean environment, simplified and cost-effective procedure, as well as clean final product.

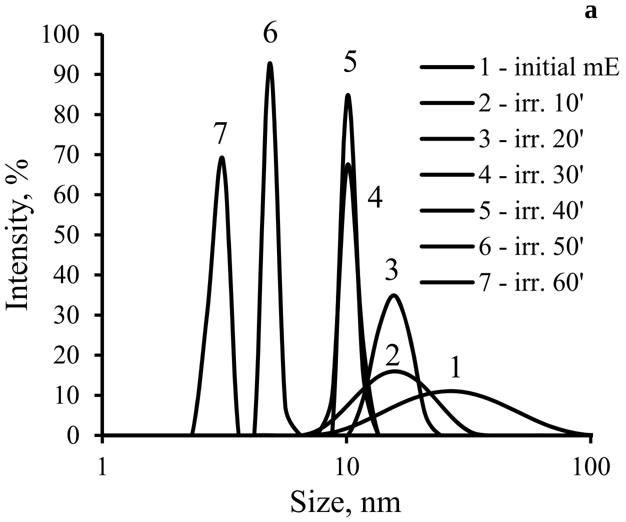
The proposed technique for AuNP synthesis is by far the most advantageous, since the O/W microemulsions are suitable alternatives because the solvent medium of such system can minimize the use of organic solvents and the reduction of gold precursor is a clean process (UV irradiation). Since almost all types of applications involve aqueous NP dispersions, and thus additional chemicals as dispersing agents, the use of O/W microemulsion template result into a one-pot synthesis of AuNP aqueous dispersions. This study can encourage various type of O/W mcroemulsionapplication as potential reaction medium for a wide pallet of metallic nanoparticles synthesis, ranging from those with pozitive reduction potential to those with negative potential.

By combining O/W microemulsion in which the gold precursor solution is a water phase component with UV irradiation technique simple and thiols stabilized AuNP, with various sizeand surface charges, have been synthesizd. The obtained AuNP, either by dispersion in pristine microemulsion or as powder, were further characterized.

3.1. AuNP synthesis in O/W microemulsion template

3.1.1. Simple AuNP synthesis

The O/W microemulsionwithgold precursor, $HAuCl_4$, as aqueous phase was subjected to an irradiation process for 60 minutes. Samples were measured every 10 minutes and the corresponding DLS results are shown in Figure 1. Initial, before the irradiation, the size of the nanodroplets $HAuCl_4$containing, in the pristine O/W microemulsion, was around 20 nm. By increasing the irradiation time to 60 min one can observe that the sizes of the micelles are decreasing very much up to 5 nm. Also, the intensity of the size peak increased substantially and the polydispersity index was high (~ 1) which indicates that polydisperseAuNP with small size were obtained, but with a high tendency of aggregation.



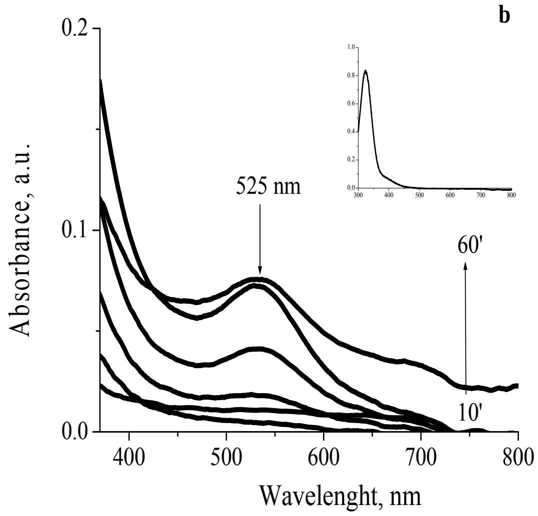


Fig. 1 Evolution in time of simple AuNP in pristine mE: (a) DLS spectra; (b) electronic spectra (the inset presents the absorption spectra of pristine O/W microemulsion)

AuNP formation in microemulsion phase was revealed also by spectroscopy measurements. The UV-Vis electronic spectra in Figure 2 shows a maximum absorbtion peak at 325 nm for initial microemulsioncharacteristic,c for [$AuCl_4^-$] ions (the inset of Figure 2), that disappears after 20 minutes of irradiation and the presence of the surface plasmon resonance (SPR) band at a 525 nm wavelength specific to colloidal AuNP evolves. These results were similar withAuNP obtained in W/O microemulsion [19]. The absorbance has limited values as the concentration and the size of the nanoparticles are small. The absorption wavelenght offers valuable information about the size of AuNP and absorbtion at 525 nm wavelenght confirms the small size of 5 nm and spherical shape [31].

3.1.2. Thiols – AuNP synthesis

As the simple AuNP were not stable in the microemulsion system, tiols (10^{-1} M) were introduced as stabilizer before the microemulsion formation. The volumetric ratio tiol: $HAuCl_4$ was 1:3.

The DLS results of the microemulsion system containing MS – $HAuCl_4$ irradiated from 0 to 240 minutes are presented in Figure 2. The DLS analysis showed that, in the synthesis process of Au-MS NP, the microemulsion template used was very stable since the sizes of the micelles were almost at the same initial value of 20 nm.

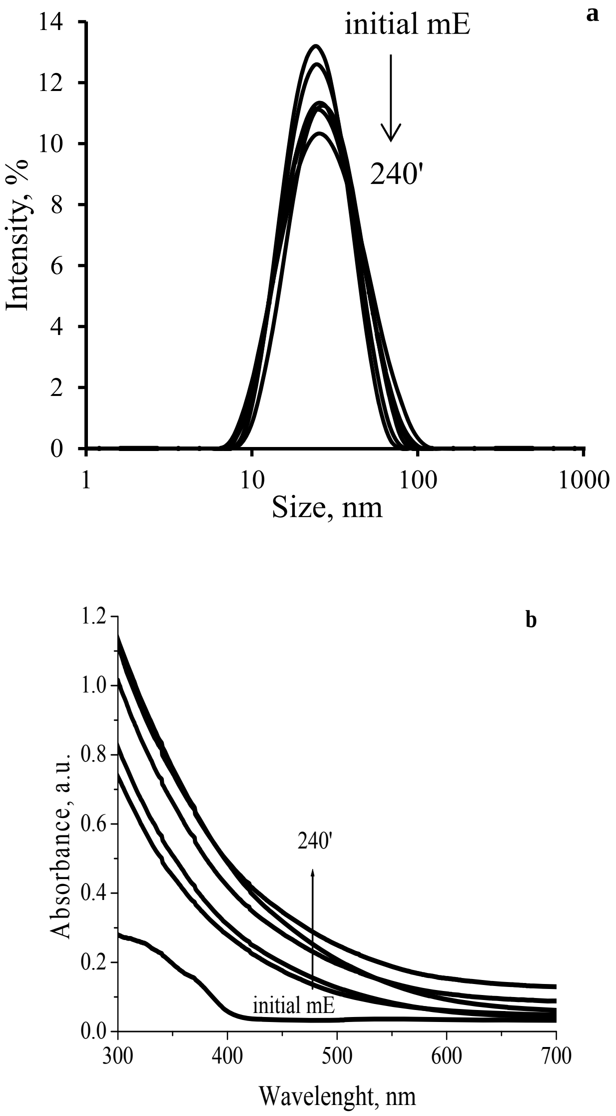


Fig. 2 Evolution in time of MS – AuNP in pristine mE: (a) DLS spectra; (b) electronic spectra

After the addition of MS thiol the intensive band specific to [$AuCl_4^-$] at 325 nm disappered and only a shoulder between 300–350 nm remains corresponding for MS derivative. The electronic spectra of AuNP functionalized with MS in a single phase synthesis in O/W microemulsion were not useful as, during the 4 hours irradiation process, the color of the microemulsion was yellow and the absorption peak specific for the plasmonresonance band was not visible.

The behavior of CS thiol was similar with the one of MS as the size of the AuNP stabilized with CS and dispersed in O/W microemulsion was maintained at initial value of 20 nm (Fig. 3).

The UV-Vis spectra were not presented as the absorption peak corresponding to the plasmon resonance band was not visible, the O/W microemulsion containing CS – AuNP having the same behaviour and colour as pristine MS – AuNPmicroemulsion. The "masking" behaviour can be explained by covering the AuNP surface with MS thiol molecules similar spectral shape being obtained by *Hussain et al.* [32] who studied the effect of water-soluble alkyl thioether over AuNP size control.

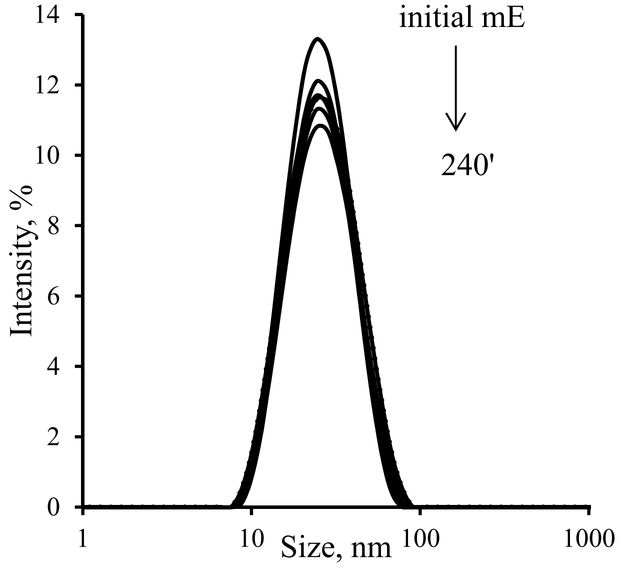


Fig. 3 Evolution in time of CS – AuNP size

The narrow shape of the size distribution indicates the homogeneity distribution of the gold precursor in the O/W microemulsion. A potential mechanism of AuNP formation and stabilization could be formulated. After the O/W microemulsion has been formed the gold precursor and thiols molecules are dispersed in continuous water phase, but after the irradiation and formation of Au-S bond between AuNP and thiols, the CS – AuNP are transfered in oil droplets due to the hidrophobic tail of CS thiols. These could be the reason for the AuNP size and geometrical shape similar with the one of oil droplets.

3.2. Characterization of tiols – AuNP

3.2.1. XRD analysis

The final gold nanoparticles stabilized with MS or CS, as powder, were subjected to XRD measurements (Fig. 4). This analysis revealed the presence of the 7 diffraction peaks that are attributed to the crystalline phases of gold, similar for both gold nanoparticles stabilized with MS or CS, at $2\,\theta = 38, 44, 64, 78, 82, 98$ and $111\ ^{o}C$ that correspond to crystalline planes (111), (200), (220), (311), (222), (400) and (311) of gold. The diffraction peaks corresponding to the diffraction planes (111), (200), and (220) were indexed to the gold metal with face centered cubic [31].

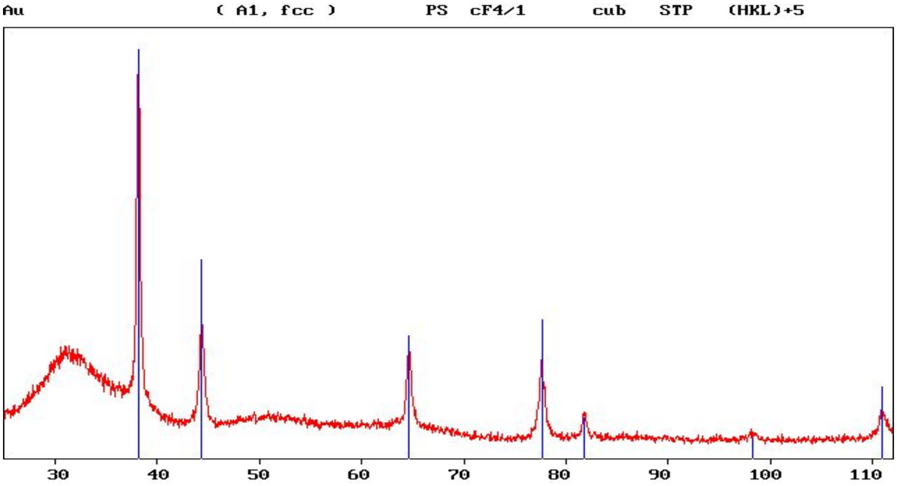


Fig. 4 XRD analysis of MS – AuNP powder

3.2.2. EDXRF analysis

In the Fig. 5 is the compositional EDXRF analysis of the powder sample containing MS-AuNP. The characteristic peaks of different elements have been drawn by existing database.

The EDXRF qualitative analysis of the solid sample of AuNP stabilized by MS thiol identified the presence of gold in a percent of 99.41%.

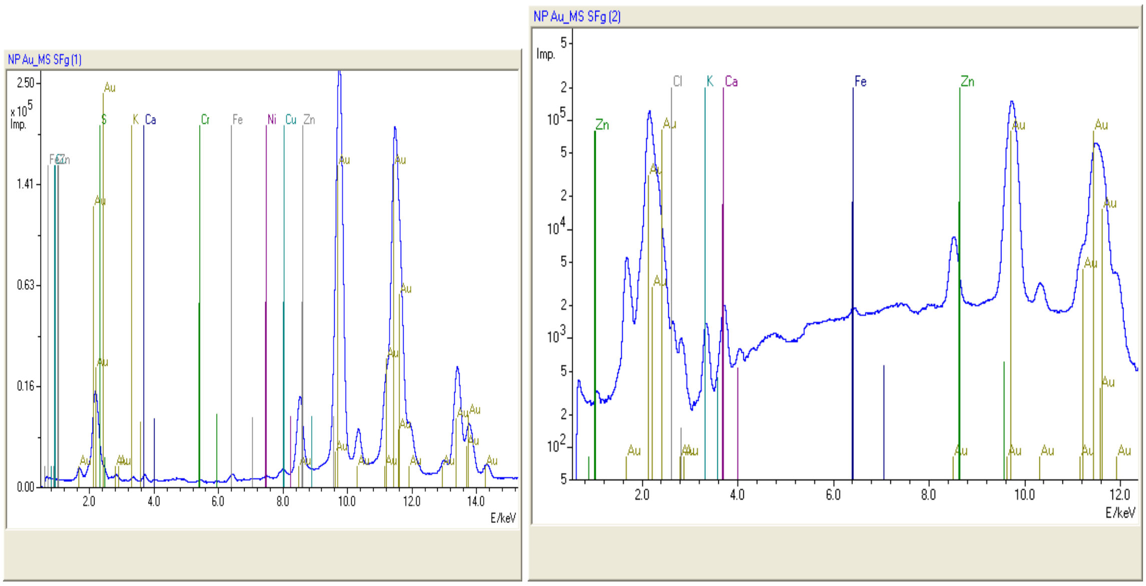


Fig. 5 EDXRF analysis of MS – AuNP powder in different conditions of the EDXRF analysis: 1 mm slot, U = 44.70 kV, I = 0.30 mA, measurement time per aquisition 180 s, number of energy channel used 2048 (left side) and 2 mm slot, U = 18.87 kV, I = 0.30 mA, measurement time per aquisition 300 s, number of energy channel used 1024 (right side).

EDXRF analysis (Figure 6) of the Au-CS NP in solid state indicated the presence of gold in a major percent, 99.54%. The overlapping of the two spectra, for the two types of samples, Au-MS and Au-CS nanopartiles, showed they have a similar composition.

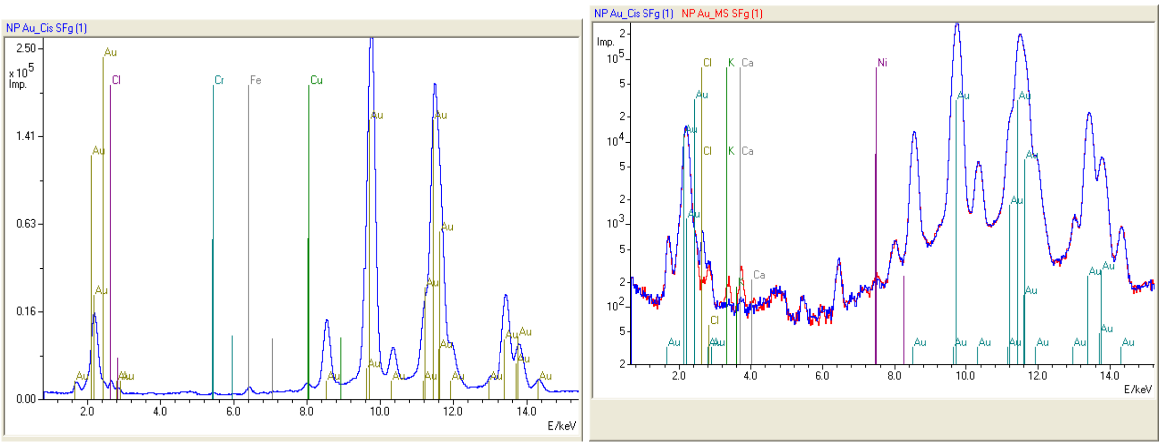


Fig. 6 EDXRF analysis of CS AuNP (left side) and overlapping MS – AuNP/CS – AuNP (right side)

3.2.3. Topografic structure

Since the two types of samples, Au-MS and Au-CS nanoparticles, seem to have similar composition, structure and size, the later was chosed for size and shape confirmation by HRTEMmeasuremens (Figure 7).

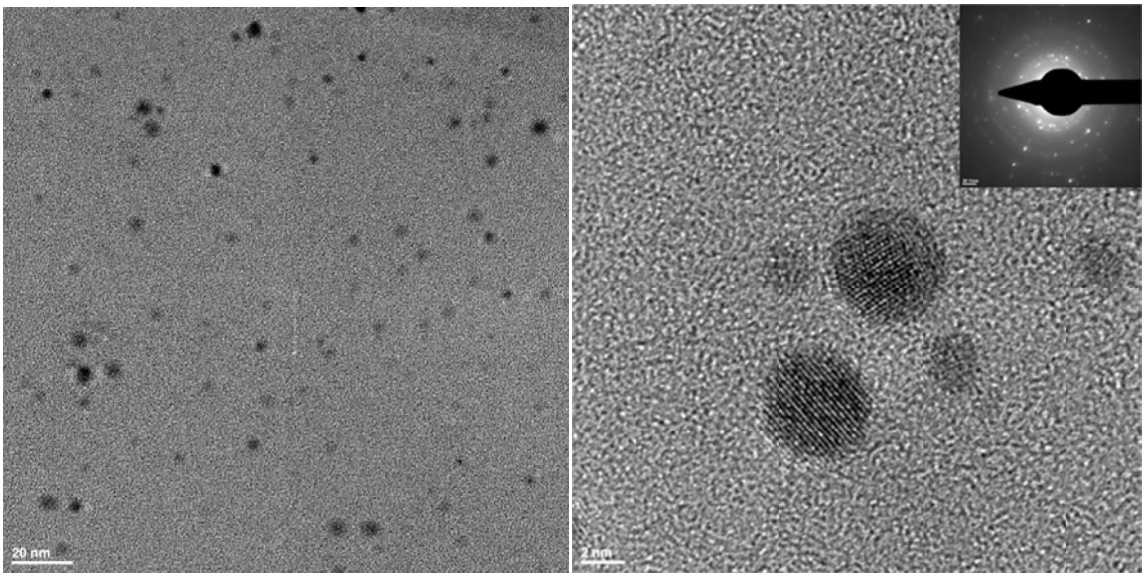


Fig. 7HR-TEM micrograph of CS – NP's (right side – magnification) and the inset showing the corresponding SAED patterns.

One can see that all AuNP are spherical in shape and well dispersed from each other and size of 5 nm smaler than the one obtained from DLS measurements. When are dispersed in O/W microemulsion the AuNP are surrounded by a surfactant molecules layer which increases the size estimated by DLS.

The SAED patterns recorded at a camera lenght of 80 nm consisted of a number of diffraction spots arranged in circular rings, indicating areas of cristalineAuNP structure.

3.2.4.Surface charge of tiols –AuNP

Pozitively and negatively AuNP surface charge have various applications in biological and medicine field such as gene delivery [33], colorimetric detection of glucose [34], inhibition of Alzheimer’s amyloid-β fibrillization [35] and binding, stabilization and delivery of therapeutic DNA, RNA and other biological macromolecules [36]. Relating to the delivery efficiency the polarity of AuNP is important, due to the higest deliverance potential displayed by pozitively charged AuNP and grater cellular uptake showed by negatively charged AuNP than neutral AuNP which was likely because of their affinity for membrane proteins [37].

Using these two ligands AuNP with different surface charges have been obtained (Table 1). Zeta Potential was the parameter used for the investigation of the surface charge of AuNP capping ligands.

Table 1 Zeta potential values indicating the positively and negatively surface charge of AuNP

No	Ligand type	Zeta potential mV	PdI
1	MS	-28.1	0.229
2	CS	+24.9	0.238

Negatively AuNP surface charges were obtained using MS, whereas pozitivelyAuNP surface charge using CS, as thiols capping ligands of gold precursor, $HAuCl_4$. The negative charge for MS and the pozitively charge in the case of CS were formed due to the free sulphate, SO_3^- and ammonium, NH_3^+ ions remained at the surface of AuNP, after the strong chemical bond between the gold and sulfur [38].

4. Conclusions

Stable AuNP with spherical shape and size of 5 nm were succesfully prepared by combining the soft chemical O/W microemulsiontemplate with physical photoreduction technique. While theAuNP synthesized in O/W microemulsiontemplate have not been stable the addition of MS and CS thiolsleads to stable nanoparticles that preserve the size and shape of pristine droplets. The size, shape and formation of AuNP were confirmed by DLS measurements, UV-Vis spectroscopy, XRD, EDXRF, SAED and HR-TEM analyses. XRD analysis revealed the 7 specific peaks at $2\ \Theta = 38, 44, 64, 78, 82, 98$ and $111\ ^{o}C$ that correspond to crystalline planes (111), (200), (220), (311), (222), (400) and (311) of gold. The EDXRF analysis confirmed the presence of Au as major component.Pozitively and negatively AuNP surface charges were obtained using CSandMS, respectively, as thiols capping ligandsof gold precursor.

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