SINTEZA ŞI CARACTERIZAREA NANOPARTICULELOR DE AUR STABILIZATE CU PVP (POLIVINILPIROLIDONĂ)
SYNTHESIS AND CHARACTERIZATION OF PVP (POLYVINYL PYRROLIDONE) STABILIZED GOLD NANOPARTICLES

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Gold nanoparticles between 2 and 5 nanometers were synthesized using an easy obtaining method with good reproducibility using PVP as protective polymer and $NaBH_4$ as reducing agent. The Au nanoparticles were characterized by TEM, XPS, XRD and UV-Vis. They are spherical with a very good dispersion making them suitable for a vast number of applications including catalytic and photocatalytic tests for nitrate and nitrite removal from water.

Nanoparticule de aur cu dimensiuni între 2 şi 5 nm au fost sintetizate folosind o metodă de obținere facilă şi cu o reproductibilitate bună, folosind PVP ca şi polimer protector şi $NaBH_4$ ca agent de reducere. Nanoparticulele de Au au fost caracterizate prin TEM, XPS, XRD şi UV-Vis. Acestea sunt sferice şi au o dispersie bună devenind astfel adecvate pentru o serie largă de aplicații, printre acestea putându-se număra teste catalitice şi fotocatalitice de reducerea a nitraților şi a nitriților din ape.

Keywords: *gold nanoparticles, synthesis, characterization*

1. Introduction

Nanoparticles are very interesting materials from scientific and practical points of view as well as with numerous applications in electronic, catalytic, biomedical or sensor fields. Great interest was focused on noble metal materials, gold being one of the most studied materials due to its optical, spectroscopic and catalytic properties [1-4]. Several preparation methods with various complexity degrees are currently available. Gold nanoparticles were obtained using azacryptand, both as reductand and stabilizer [3]. They were reduced directly in an environmentally friendly synthesis using tannic acid [5] or by seed-mediated approach in aqueous media using cetyltrimethylammonium bromide (CTAB) [6]. Some other methods include the use of Gemini surfactants as ligands [2] or reduction by photochemical synthesis using a photochemical initiator [7]. Other researches demonstrated the possibility of obtaining gold nanoparticles using peptide–biphenyl hybrids (PBHs) as capping agents [1] or via a burst nucleation of Au upon injection of the reducing agent *t*-butylamine-borane complex into a 1,2,3,4-tetrahydronaphthalene solution of $HAuCl_4 \cdot 3H_2O$ in the presence of oleylamine [8]. One of the most convenient and versatile procedure of synthesis consists in the use of a polymer as a protective agent. The polymers control the dimension of the nanoparticles and also offer a good dispersion [9-11].

The aim of the present paper was to obtain very small gold nanoparticles, under 5 nm, using a facile synthesis method based on the polymer approach. They need to be very small because later they will be deposited on an oxide substrate and will be used as potential catalysts and photocatalysts in the nitrate and nitrite removal from water. The obtaining conditions and the influence of some parameters on nanoparticles formation were studied along with their characterization.

2. Experimental

Chloroauric acid ($HAuCl_4 \cdot 4H_2O$) was provided by Wako Pure Chemical Industry, Ltd., PVP (polyvinyl pyrrolidone) with molecular weight of 8000 and sodium borohydride ($NaBH_4$) from Alfa Aesar GmbH . All the solutions for the synthesis of gold nanoparticles in this paper were freshly prepared using demineralised water.

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The as obtained nanoparticles were characterized through TEM microscopy. Transmission electron microscopy (TEM) was performed on FEI Tecnai G2-F30 S-Twin field-emission gun scanning transmission electron microscope (FEG STEM) operating at 300 kV. A drop of the nanoparticles suspension was mounted on a holey carbon film copper grid allowing the solvent to evaporate at room temperature. The XRD patterns were collected by means of a Rigaku diffractometer type Ultima IV in parallel-beam geometry. The source of the X-rays was a Cu tube (λ = 0.15418 nm) operating at 40 kV and 30 mA. Counts were collected from 10º to 80º with a step size of 0.02 and a speed of 5º/min. Rigaku's PDXL software package, connected to the ICDD database was used for the phase identification. UV-VIS spectra were performed using an Analytic Jena Specord 200 plus apparatus. The XPS analysis was carried out with a VG Esca 3 Mk II spectrometer using an Al Ka radiation source at 1486.7 eV. The 100-mm radius hemispherical electron analyzer was operated at a pass energy of 50 eV. The experimental spectra were fitted with Voight functions (SDP 2.3).

In this work, very small particles, up to 5 nm were obtained. Well-dispersed, uniform Au nanoparticles protected with PVP have been synthesized by a modified Tsukuda protocol [12]. To control the particles growth and avoid the particle agglomeration as well as to obtain narrow size distribution, PVP (polyvinyl pyrrolidone) was used as protective polymer and $NaBH_4$ as reducing agent.

The gold precursor consisted in a water based solution of chloroauric acid of 1.8 mM. This was added in a water based solution of PVP, 44 mM according to Figure 1. Namely 25 ml of Au solution was added in 50 ml of PVP solution and they were kept under stirring at 0 °C for one hour. The reducing agent was a water based solution of $NaBH_4$. Thus 10 ml of sodium borohydride solution of 16.5 mM was injected rapidly in the Au^{3+}/PVP mixture. The solution turns dark red almost immediately therefore the reduction took place. The obtained mixture was kept under stirring for another half of hour for a better homogenization and then the synthesized nanoparticles were recovered. The recovery can be done in two ways. One consists in adding in the reduced solution a quantity of acetone, equal to the volume already present in the reaction flask and then to keep it in the freezer for several days. The nanoparticles will settle at the bottom of the flask and their recovery can then be easily made. Another way, with faster results, could be by using a 10.000 RPM centrifuge device. After separation, the obtained powder was calcinated at 200 °C for 2 hours. After recovery, all the samples were characterized through TEM, XRD and XPS analyses. UV-Vis spectrum was obtained for the prepared solution prior to nanoparticle recovery.

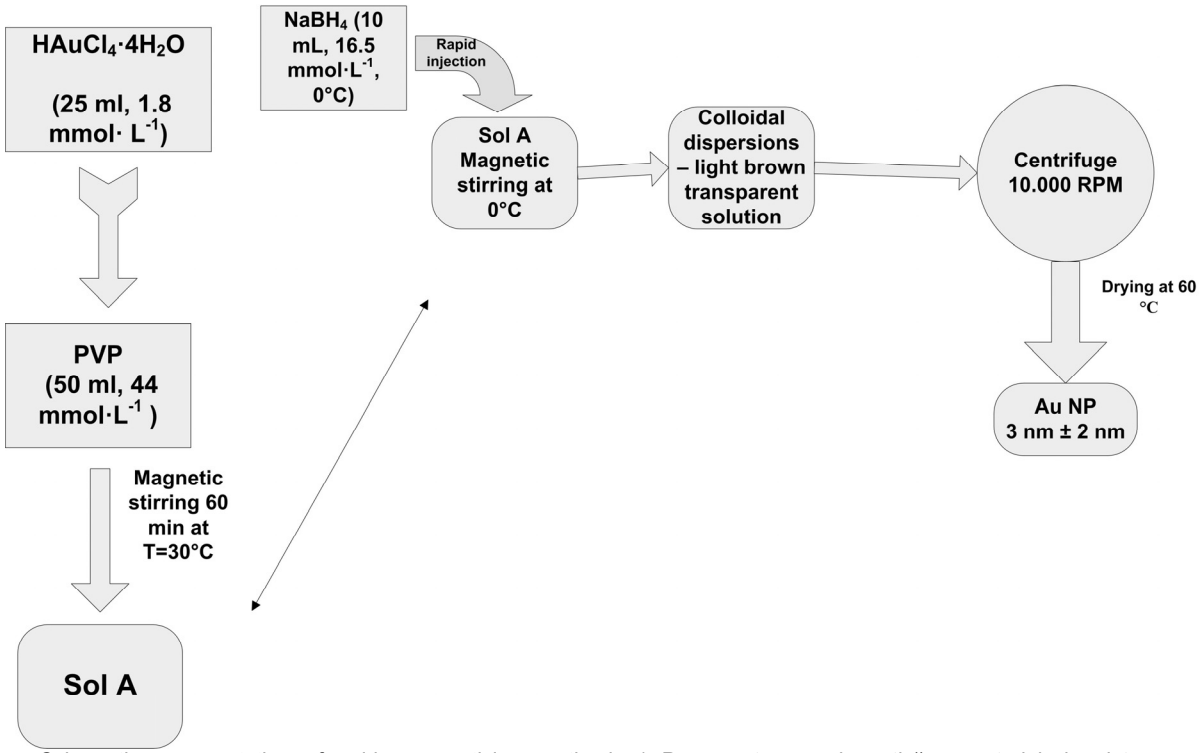

Fig. 1 - Schematic representation of gold nanoparticles synthesis / *Reprezentarea schematică a metodei de sinteza pentru nanoparticulele de aur obținute.*

3. Results and discussions

After reduction and before nanoparticle recovery the obtained gold solution was analysed by UV-Vis spectroscopy (Figure 2). It can be seen that the synthesized gold nanoparticles have some adsorption in the visible range, suggesting that they can be used in further experiments as photocatalysts.

TEM analysis was used to see the shape, size and the morphology of the synthesized gold nanoparticles. It was observed that the as obtained Au/PVP nanoparticles are very small and spherical, with a size ranging between 2 and 5 nm (Figure 3).

The HRTEM image in the insert in Figure 3a reveals the structure of crystalline Au nanoparticles. The lattice fringe distance of ~0.234 nm exhibited by the nanocrystalline particles correspond to Au (111) plane (JCPDS card no. 03-065-8601). The HRTEM results are in good agreement with XRD results.

In order to make sure of their composition, the synthesized gold nanoparticles were subjected to X-Ray diffraction analysis. Figure 4 shows the XRD pattern of Au/PVP sample. The XRD pattern reveals the presence of diffraction lines which can be assigned to crystalline gold cubic phase according to (JCPDS card no. 00-004-0784). The

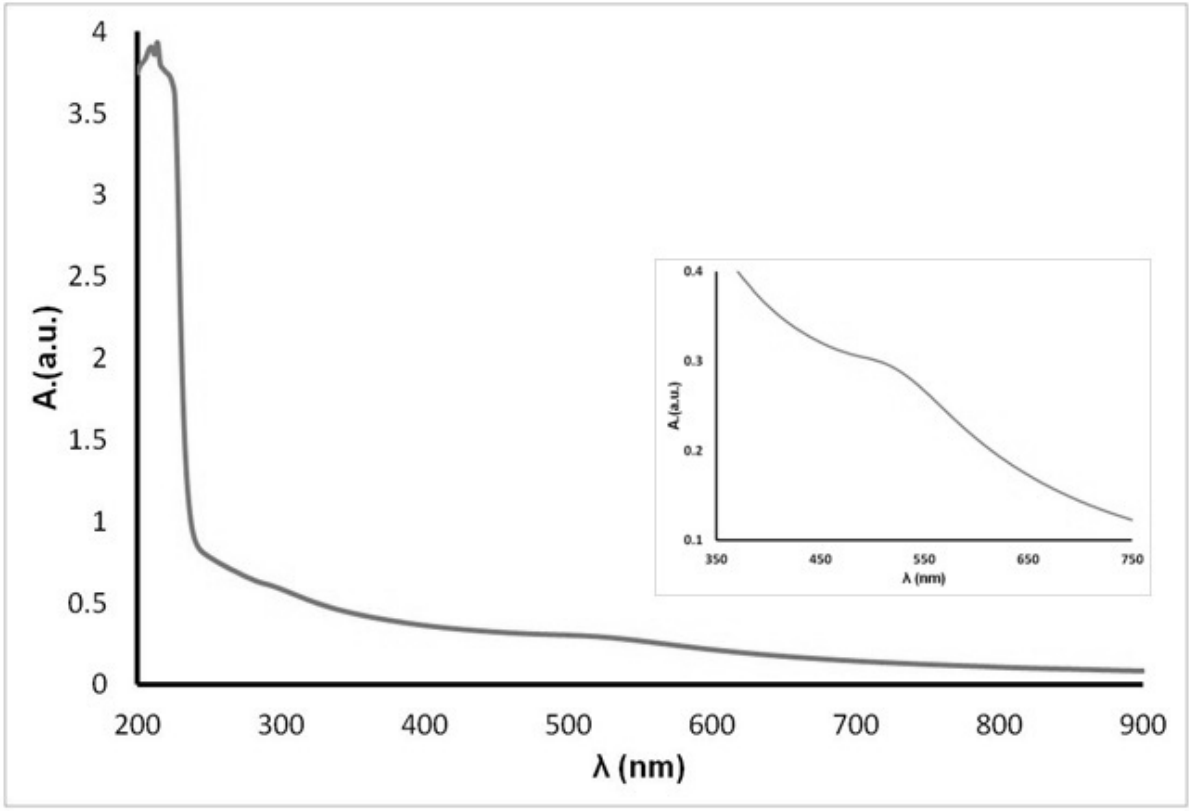

Fig. 2 - UV-Vis spectrum of Au/PVP sample. Detail of the visible range in the bottom right corner / *Spectrul UV-Vis al probei Au/PVP. Detaliu al zonei vizibile în colțul din dreapta jos.*

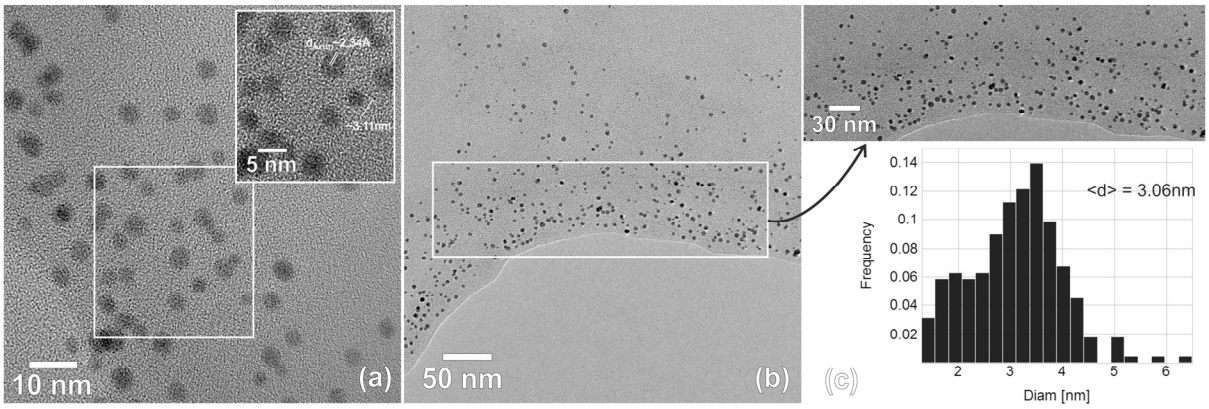

Fig. 3 - TEM images of the obtained gold nanoparticles, (a) detail at 10 nm scale, (b) overview at 50 nm and (c) histogram *Imagini TEM ale nanoparticulelor de aur obținute, (a) detaliu la o scală de 10 nm, (b) imagine de ansamblu la 50 nm, (c) histograma.*

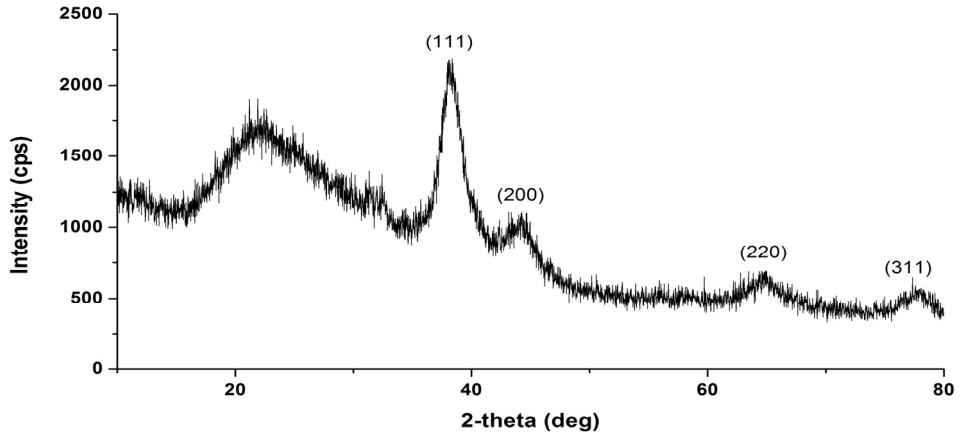

Fig. 4 - XRD spectrum of the synthesized gold nanoparticles.
Spectrul XRD al nanoparticulelor de aur sintetizate.

Table 1

The results of the XRD pattern refinement / *Rezultatele XRD*

2 theta - (deg.)	(h k l)	FWHM (deg.)	Size (Å)	d- spacing (Å)	Lattice parameter a=b=c (Å)	V (Å3)	Rwp	S
38.08	(111)	2.3577	37.23	2.3609	4.0633	67.09	7.83	1.1506
44.36	(200)	2.9561	30.31	2.0410				
64.81	(220)	5.3562	18.35	1.4374				
78.03	(311)	5.3562	19.94	1.2235				

Where: (h k l) are Miller indices; FWHM is the full width at half maximum of the intensity; (V) is the unit cell volume; S is goodness of the fit; and Rwp- measurement deviation with the weight and profile function.
Unde: (h k l) sunt indicii Miller; FWHM reprezintă semi lărgimea benzii; (V) reprezintă volumul; S corectitudinea fitării; şi Rwp – deviația măsurată

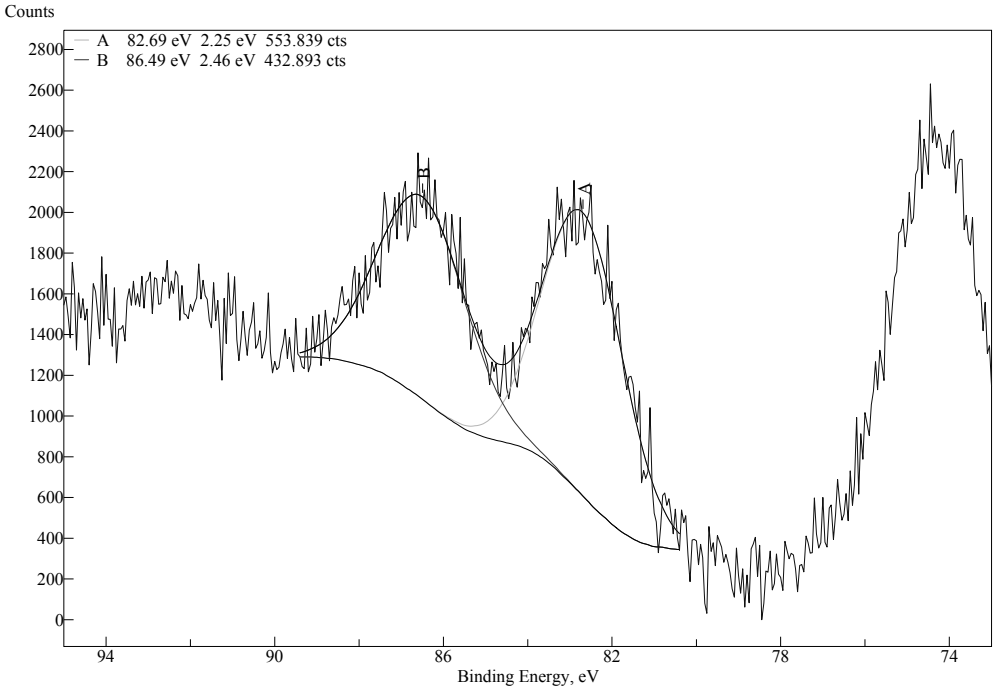

Fig.5 - XPS spectrum of the synthesized gold nanoparticles / *Spectrul XPS al nanoparticulelor de aur sintetizate.*

four diffraction lines corresponding to the (111), (200), (220) and (311) gold planes appear at 2θ positions 38.08º, 44.36º, 64.81º and 78.03º respectively. No other diffract ion lines due to the presence of impurities were observed. The broad halo at around 2θ=21º in the diffraction pattern is the contribution of glass sample holder.

The difraction lines are considerably broadened; the extent of broadening is described by full width at half maximum intensity of the peak (FWHM). This broadening of the diffraction peak is related to the size of nanoparticles via the Scherrer's formula:

$$D=k\cdot \lambda / (FWHM)\cdot\cos(\theta) \quad (1)$$

Where: κ is a shape factor (taken as 0.94), FWHM is the full width at half maximum of the intensity vs. 2θ profile λ is the wave length of the Cu Kα radiation (1.54056 Å) and θ is the Bragg's diffraction angle.

The XRD pattern was refined by Whole Pattern Powder Fitting (WPPF) method) using PDXL software. The fitting was performed using the split pseudo-Voigt profile function and B-spline background model. The fitting quality of the experimental data was checked by using the following criteria: the goodness of fit S that should be closed to 1 for a good fit and Rwp (weighted differences between measured and calculated values) that should be closed to or less than 10%.The parameters obtained from the XRD pattern are listed in the Table 1.

The lattice parameter of gold nanoparticles equals to 4.0633 Å, is smaller than 4.0786 Å of that given in JCPDS card no. 00-004-0784 there seems to be a lattice contraction.

As a supplementary analysis an XPS spectrum was performed. Two peaks are present at about 82.7 eV (peak A) and 86.5 eV (peak B) suggesting that gold is present at the surface, the binding energy being characteristic to Au4f (Figure 5).

Fig.1 -.

Fig.2 - Fig.3 - Fig.4 - Fig.5 -

4. Conclusions

Very small gold nanoparticles were successfully obtained using a modified Tsukuda protocol with PVP (polyvinyl pyrrolidone) as protective polymer. The as obtained nanoparticles were characterized by various methods (TEM, XPS, and XRD) to elucidate the relationship between morphology and preparation variables. It was found that they are spherical with a size between 2-5 nm. Their adsorption in the UV-Vis spectra is rather poor but they have a very good dispersion as it could be seen from the TEM images. Therefore, these particles can have a vast number of applications, including their use in photocatalytic and catalytic tests. Due to the fact they are very small and they possess a very good dispersion they make good candidates if used alone [13] or together with some other known catalytic metals, like palladium [14,15] and after deposition on a photocatalytic or catalytic active oxide, like TiO_2 [16,17], as mono and bimetallic catalyst in nitrate and nitrite removal from water [18,19].

***Acknowledgement**: This work was supported by PN2 100 INTEGRATREAT and PN2 46 BICLEANBIOS. The work of Razvan State is supported from Project SOP HRD - PERFORM /159/1.5/S/138963.*

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