PREPARATION OF GOLD AND SILVER NANOPARTICLES BY MECHANOCHEMICAL ACTIVATION

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ABSTRACT

Nanoparticles of gold and silver were synthesized by milling of dry mixtures of hydrophilic polymers and $AgNO_3$ (or $HAuCl_4$) at 650 rpm. As hydrophilic polymers poly(N-vinylpyrrolidone) (PVP), poly(ethyleneglycol) (PEG), poly(vinyl alcohol) PVA, poly(acrylic acid) (PAA) and poly(N,N-dimethyl-N,N-diallylammonium chloride) (PDMDAAC) were used. It was found that the content of metals nanoparticles depends on milling time. The dispersed in aqueous solution gold and silver nanoparticles show the surface plasmon resonance at λmax = 310 nm (Au) and 430 nm (Ag). XRD analysis revealed that the average size of nanoparticles is in the range of 20-40 nm. The content of Ag nanoparticles depends on the concentration of OH groups of polymers and changes in the following order: PVA (38%) > PEG (28%) > PVP (15%). The amount of gold nanoparticles obtained in the presence of PAA and PEG is equal to 73 and 67% respectively. Nanoparticles of metals can be used as nanocatalysts for hydrogenation and oxidation of organic substrates.

Key words: gold and silver nanoparticles, hydrophilic polymers, mechanochemical activation

INTRODUCTION

Nanoparticles have received much attention due to unique size dependent properties. Nanoparticles of gold and silver possess optical, antibacterial and catalytic properties [1]. To date, a number of procedures for synthesis of gold and silver nanoparticles have been reported, of which the most widely used are wet chemistry techniques based on chemical reactions in solution that yield metal nanoparticle colloids with a wide range of sizes, shapes, and dielectric environments [2]. Stable gold and silver colloids were prepared by the *in situ* reduction of tetrachloroauric acid ($HAuCl_4$) and silver nitrate ($AgNO_3$) in the

presence of protective nonionic, anionic and cationic polymers [3-7]. Earlier [8] a dry solid-state high-speed vibration milling method for the synthesis of silver nanoparticles in the presence of poly(vinylpyrrolidone) (PVP) has been reported. In the present communication we have extended this method for synthesis of silver and gold nanoparticles.

SAMPLE PREPARATION AND ANALYSIS

Aqueous solution of $HAuCl_4$ with concentration of 0,5mg/mL and solid $AgNO_3$ were used for preparation of nanoparticles. As polymer protecting agents a series of hydrophilic polymers – poly(N-vinylpyrrolidone) (PVP), poly(ethyleneglycol) (PEG), poly(vinyl alcohol) PVA, poly(acrylic acid) (PAA) and poly(N,N-dimethyl-N,N-diallylammonium chloride) (PDMDAAC) were selected. Gold nanoparticles were prepared as follows: 100 mg of PVP, (PAA and PEG) were dissolved in 5 mL of $HAuCl_4$, dried in open air then in oven at 313K. The dried films of polymer and $HAuCl_4$ were placed to ball mill "Retsch PM 200" (Germany) and vigorously milled at 650 rpm during 1 h at room temperature. The same procedure was used for the mixture of dry $AgNO_3$ and polymer powders. For removal of excess amount of polymer the crumbled mixtures were suspended in water and centrifugated on preparative centrifuge "Eppendorf Centrifuge 5810R" (Germany) at 5000 rpm. After decantation the solid residue was dried in oven at 313K. XRD spectra were registered on "X,pert MPD PRO" (Holland) at room temeprature. UV-Vis spectra of dispersed aqueous solution of nanopartciles were recorded on spectrophotometer "UV-Mini" (Japan).

RESULTS AND DISCUSSION

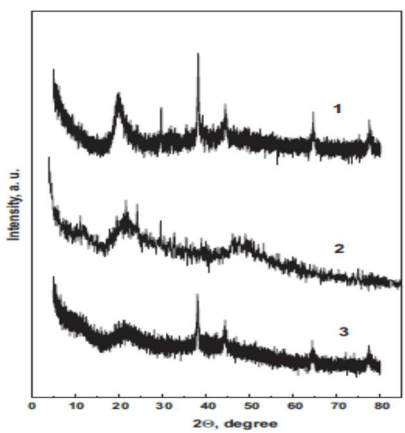

Fig. 1 – XRD patterns of Ag nanoparticles obtained in the presence of PVA (1), PEG (2) and PVP (3)

XRD spectra of Ag and Au nanoparticles synthesized in the presence of various polymers are shown in *Figure 1* and *Figure 2*. Diffraction peaks at 2θ = 38,29; 44,5; 64,76 и 77,8 with interplanar spacing 2,34; 2,03; 1,43 и 1,22 Å corresponds to cubic centered (fcc) lattice of silver nanoparticles (111), (200), (220) и (311) (*Table 1*). These results are in good agreement with data of authors [8]. XRD analysis revealed that the average size of silver nanoparticles is in the range of 20-40 nm. The content of Ag nanoparticles depends on the concentration of OH groups of

polymers and changes in the following order: PVA (38%) > PEG (28%) > PVP (15%) (*Table 2*).

Table 1 – Lattice parameters of silver nanoparticles

Sample	*h*	*k*	*l*	d, [Å]	2θ, degree
PVP-Ag^0	1	1	1	2,3487	38,291
	2	0	0	2,0340	44,508
	2	2	0	1,4383	64,764
	3	1	1	1,2266	77,805

Table 2 – Results of elemental analysis of silver nanoparticles

Silver compounds, %	Polymer		
	PVA	PEG	PVP
Ag	38	28	15
Ag_2O	21	1	13
AgO	8	1	10
Other silver compounds	33	70	62

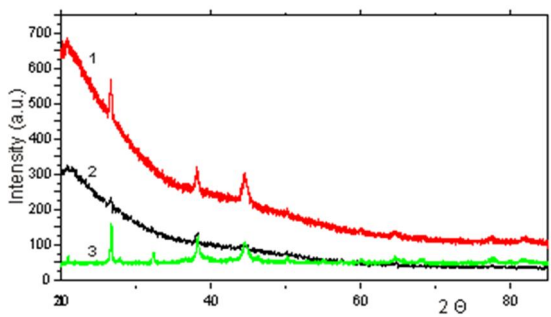

Fig.2 – XRD spectra patterns of Au nanoparticles obtained from the mixture of PVP and $HAuCl_4$ after milling during 65 min (1), 20 min (2) and after washing of precipitate (3)

It is supposed that OH groups of polymers participate in reduction of Ag^+ to Ag^0.

As seen from *Figure 2* XRD spectra of Au nanoparticles exhibit diffraction peaks at 2Θ = 38 and 45° that belong to gold nanoparticles. The amount of gold nanoparticles obtained in the presence of PAA and PEG was equal to 73 and 67% respectively. The absorption maximum of Ag and Au nanoparticles was centered at 429 and 310 nm respectively.

CONCLUSIONS

It was shown that the solid-phase high-speed vibration milling method is simple, one-step and may result in preparation of both silver and gold nanoparticles. The role of polymers is protecting of metal nanoparticles from aggregation. Functional groups of polymers are participated in reduction of tetrachloroauric acid and silver nitrate.

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