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Synthesis, Characterization and Catalytic Property of Polymer Protected Gold and Silver Nanoparticles

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Gold (AuNPs) and silver (AgNPs) nanoparticles protected by hydrophilic polymers were prepared by "one-pot" synthetic protocol. Absorption spectra, size, morphology and structure of obtained nanoparticles were investigated by UV-Vis spectroscopy, dynamic light scattering (DLS), and transmission electron microscopy (TEM). The catalytic activity of polymer-protected AuNPs and AgNPs supported on the surface of aluminum oxide was evaluated with respect to decomposition of hydrogen peroxide.

Keywords: Gold and silver nanoparticles, Hydrophilic polymers, Aluminium oxide, Catalysis.

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1. INTRODUCTION

AuNPs and AgNPs have attracted significant attention of researchers because of their unique optical, electrical, biomedical and catalytic properties [1-3]. A lot of polymers possessing nonionic, anionic, cationic and amphoteric nature are widely used as protecting agents of AuNPs and AgNPs for preventing of nanoparticles aggregation [4]. Earlier [5] we have studied the catalytic activity of AuNPs with respect to hydrogenation of 4-nitrophenol. It was found that polymer-protected AuNPs convert 4-nitrophenol to 4-aminophenol with high yield (97-99% conversion).

In the present communication we stabilized AuNPs and AgNPs by a series of hydrophilic polymers in both aqueous and organic solvents. The absorption spectra, size, and morphology of AuNPs and AgNPs were determined. The catalytic activity of AuNPs and AgNPs deposited on Al_2O_3 by impregnation method was evaluated with respect to hydrogen peroxide decomposition.

2. EXPERIMENTAL

2.1 Materials

Standard aqueous solution of tetrachloauric acid $HAuCl_4$ with concentration 100 mg·L^{-1} was purchased from Sigma-Aldrich. As polymeric stabilizing agents were used poly(N-vinylpyrrolidone) (PVP) with $M_n = 10{\cdot}10^3$, $30{\cdot}10^3$, $40{\cdot}10^3$, $350{\cdot}10^3$, β-cyclodextrin (β-CD), poly(N,N-dimethyl-N,N-diallylammonium chloride) (PDMDAAC) (20 % aqueous solution). Organic solvents – dimethylsulfoxide (DMSO, purity is 99,8%), dimethylformamide (DMF, purity is 99,5%), inorganic supporter – aluminium oxide purchased from Aldrich were used without additional purification.

Methods.

Absorption spectra of AuNPs and AgNPs were determined at room temperature by UV-Vis spectroscopy (Specord 210 plus BU, Germany). The size of nanoparticles was determined with the help of DLS device Malvern Zetasizer Nano ZS90 (UK). Concentration of Au in supernatant was determined by ion-coupled plasma atomic emission spectroscopy ICP-AES "Optima 5100DV" (Perkin Elmer, USA). Scanning electron microscopy (SEM) image was recorded on a JEOL JSM–6490LA (Japan). Transmission electron microscope (TEM) measurement was carried out with on ADX-2500 X-Ray diffraction instrument.

2.2 Synthesis of AuNPs and AgNPs

AuNPs stabilized by PVP or PDMDAAC were obtained by "one-pot" synthetic protocol [6]. For instance, aqueous solutions of $HAuCl_4$ (5 mL), 0.5 M KOH (4 mL), and 4% PVP (5 mL) were mixed, stirred and heated up to 100 °C during several minutes. As a result the colored solutions of AuNPs stabilized by PVP (PVP-AuNPs) or PDMDAAC (PDMDAAC-AuNPs) were obtained as shown in Fig.1.

For synthesis of AgNPs, 2 mmol (or 0034 g) $AgNO_3$ and 0,034 g PVP (or β-CD) were dissolved in 10 mL DMF (or DMSO, water-ethanol (50:50 vol.%) mixture) at room temperature and heated up to 180-185^{0}C for several minutes until the color of solution changed into dark brown. DMSO solution of AgNPs was kept in dark place until changing of color from colorless to khaki (dirty green), which evidences the formation of silver nanoparticles (see Fig.1).

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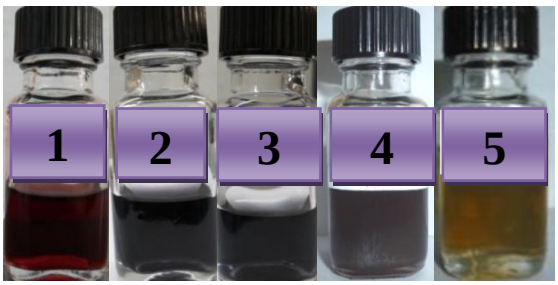
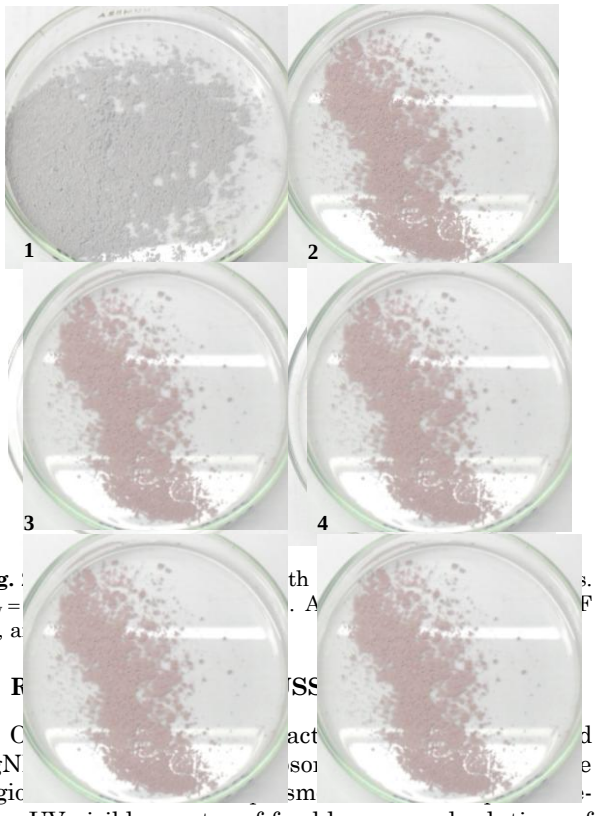


Fig. 1 – Samples of AuNPs stabilized by PVP with $M_n = 10 \cdot 10^3$ (1), $40 \cdot 10^3$ (2) and $350 \cdot 10^3$ (3) and AgNPs protected by PVP in DMF (4) and DMSO (5)

PVP-AuNPs and PVP-AgNPs were supported on Al_2O_3 by impregnation method. For this 0.5 g of Al_2O_3 was added to 5 mL of PVP-AuNPs (or PVP-AgNPs) and stirred during 5 hours. The precipitate was separated by preparative centrifuge "Eppendorf 5810R" (Germany) at $10 \cdot 10^3$ rpm, then it was washed out 5 times with distilled water. The content of Au and Ag in supernatant was determined by the ICP-AES. The precipitate was dried at 50 °C. The powders of Al_2O_3 with supported PVP-AuNPs (Al_2O_3/PVP-AuNPs) and PVP-AgNPs (Al_2O_3/PVP-AgNPs) were used as catalysts for decomposition of H_2O_2 (Fig.2).



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non. UV-visible spectra of freshly prepared solutions of AgNPs and AuNPs in the presence of water soluble polymers are depicted in Figs.3 and 4. The presence of AgNPs and AuNPs is easily detected with the bands at 420-450 nm and at 520-550 nm respectively. However, the maximum of absorption of AgNPs in DMSO appears at 500 nm and can be explained by differences in shapes and dimensions of nanoparticles.

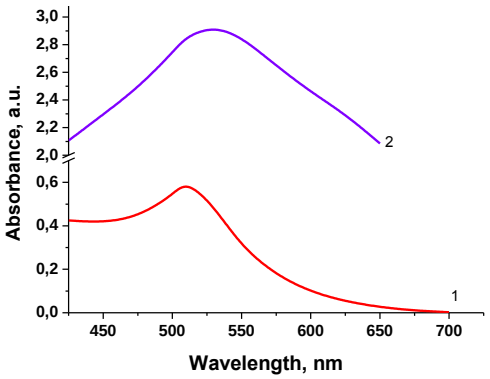

Fig. 3 – Visible spectra of AuNPs stabilized by PDMDAAC (1) and PVP (2)

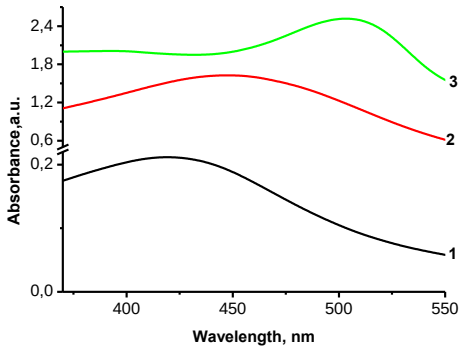

Fig. 4 – Visible spectra of AgNPs stabilized by PVP in H_2O-C_2H_5OH (1), DMF (2) and DMSO (3)

Fig.5 represents the size distribution of AuNPs-PVP. In dependence of the molecular weights of PVP the sizes of PVP-AuNPs is varied from 10 to 25 nm. It seems that optimal molecular weight of PVP leading to

AuNPs with average size 10 nm is $40 \cdot 10^3$. Surface charge of AuNPs-PVP is negative and equal to –2.03 mV.

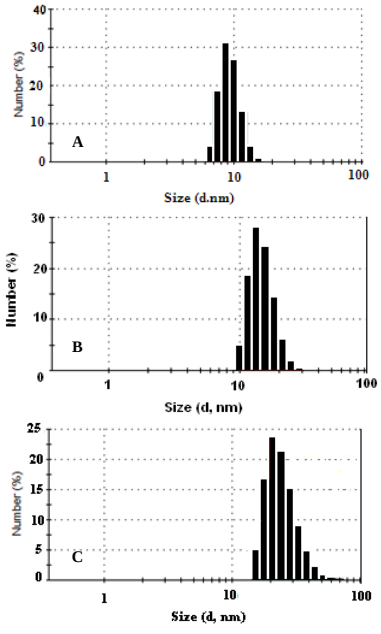

Fig. 5 – Size distributions of AuNPs stabilized by PVP with $M_w = 10 \cdot 10^3$ (A) $40 \cdot 10^3$ (B) and $350 \cdot 10^3$ (C)

SEM pictures of PVP-AuNPs before and after deposition on the surface of Al_2O_3 are shown in Figs. 6 and 7.

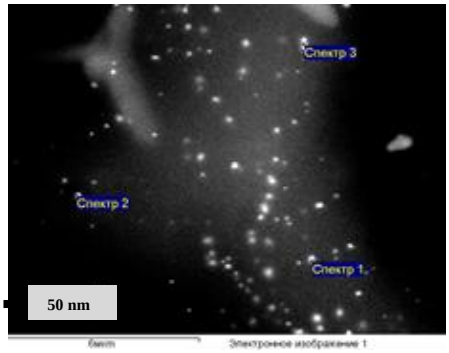

Fig. 6 – SEM pictures of pristine PVP-AuNPs

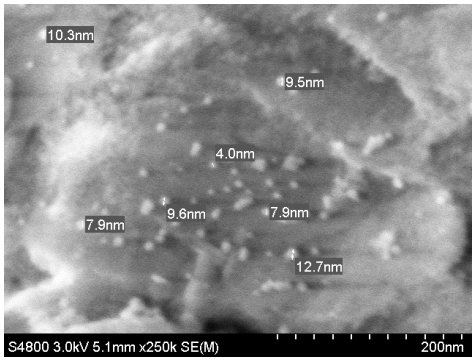

Fig. 7 – SEM pictures of PVP-AuNPs supported on aluminum oxide

As seen from the SEM image the average size of AuNPs before (white sparkling dots) and after deposition on Al_2O_3 (white dots) is in the range of 10-20 nm and coincides well with DLS data.

TEM image of AuNPs-PVP deposited onto Al_2O_3 reveals that there are no big agglomerates of the gold nanoparticles (Fig.8). TEM micrograph clearly shows the attached to the surface of Al_2O_3 gold nanoparticles with average size varying from 10 to 25 nm. TEM results are in good agreement with hydrodynamic sizes of AuNPs measured by DLS and SEM results.

Fig.9 represents the size distribution of AgNPs-β-CD in DMSO, AgNPs-β-CD in DMF, and AgNPs-PVP in DMF. In dependence of polymer and solvent nature the sizes of polymer-protected AgNPs is varied from 7 to 25 nm.

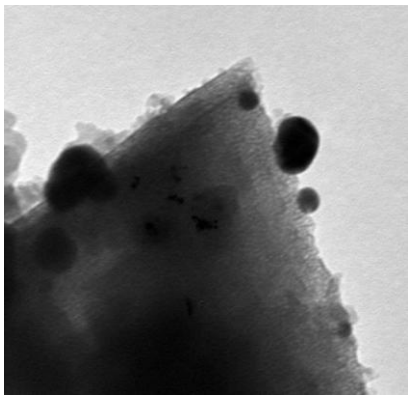

Fig. 8 – TEM image of PVP-AuNPs supported on Al_2O_3

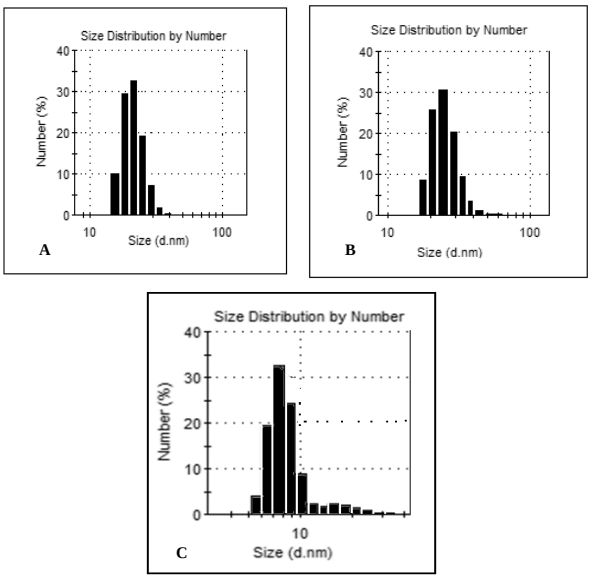

Fig. 9 – Size distributions of AgNPs stabilized by β-CD (A,B) and PVP (C) in DMSO (A) and DMF (B, C)

Table 1 shows the ζ-potentials of AgNPs stabilized by PVP and β-CD in DMSO and DMF. It is seen that the ζ-potentials of AgNPs in DMSO and DMF are positive and negative respectively.

Table 1 – The ζ-potentials of AgNPs stabilized by PVP and β-CD in DMSO and DMF

Polymer	Solvent	ζ-potential, mV
PVP	DMSO	+1,3
	DMF	–0,267
β-CD	DMSO	+3,93
	DMF	–0,331

The catalytic activity of AuNPs depends on the size and amount of gold nanoparticles deposited on the surface of Al_2O_3. It was found that in dependence of the molecular weight of PVP the size distribution of PVP-AuNPs is varied from 10 to 25 nm. The concentration of Au nanoparticles deposited on Al_2O_3 is very small and equal to 0.06-0.1%. As illustrated in Fig.10, the rate of H_2O_2 decomposition increases exponentially while Al_2O_3 itself and PVP supported onto Al_2O_3 do not show any catalytic activity in decomposition of H_2O_2.

It should be noted that in the presence of Al_2O_3/AuNPs-PVP the rate of H_2O_2 decomposition exhibits an induction period that depends on the molecular weight of PVP and changes in the following order PVP-$350{\cdot}10^3$ > PVP-$40{\cdot}10^3$ > PVP-$10{\cdot}10^3$. As seen from Fig.10, decomposition of H_2O_2 in the presence of Al_2O_3/AuNPs-PVP-$350{\cdot}10^3$ starts after 1 h while the same reaction starts immediately in the presence of Al_2O_3/AuNPs-PVP-$10{\cdot}10^3$. This is probably explained by less accessibility of gold nanoparticles to substrate due to surrounding of catalytic centers by high molecular weight PVP. The catalytic activity of Al_2O_3/AgNPs-PVP was also checked with respect to H_2O_2 decomposition. As seen from Fig. 10B AgNPs have much lower catalytic activity than that of AuNPs.

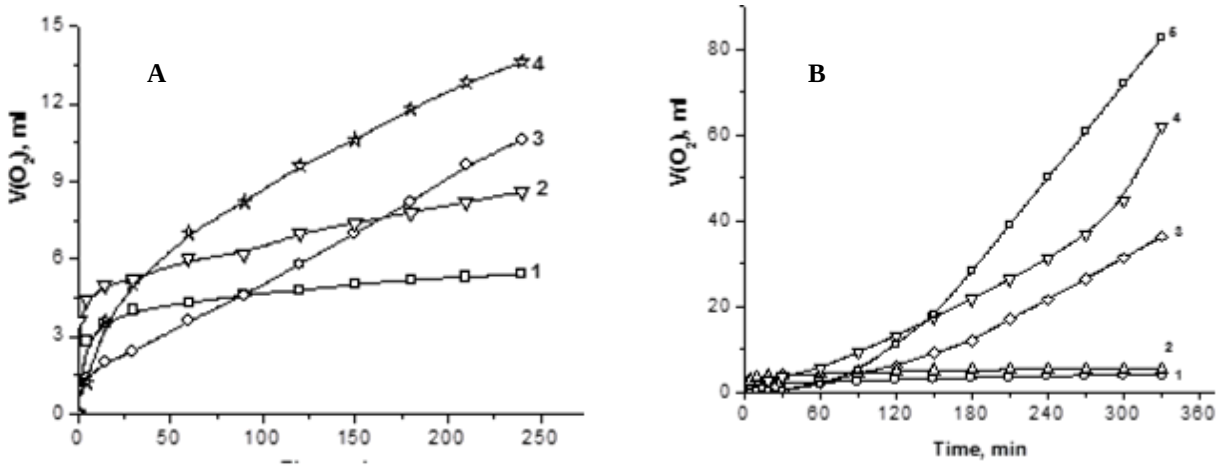

Fig. 10 – Catalytic activity of supported on aluminum oxide AuNPs and AgNPs with respect to H_2O_2 decomposition. **A.** PVP $40{\cdot}10^3$/ Al_2O_3 (1), PVP $40{\cdot}10^3$ (2), PVP $40{\cdot}10^3/Al_2O_3$/AuNPs (3), PVP $10{\cdot}10^3/Al_2O_3$/AuNPs (4) , PVP $350{\cdot}10^3$/ Al_2O_3/AuNPs (5). **B.** AgNPs deposited on Al_2O_3 (1) and synthesized in DMF (2), H_2O-C_2H_5OH (3) and DMSO (4)

4. CONCLUSIONS

Polymer-protected gold and silver nanoparticles were synthesized by "one-pot" method and characterized by UV-Vis-spectroscopy, DLS, SEM and TEM methods. The average size of AuNPs stabilized by PVP is varied from 10 to 25 nm. In dependence of polymer and solvent nature the average size of polymer-protected AgNPs is varied from 7 to 25 nm. Polymer-protected gold and silver nanoparticles were supported on the surface of Al_2O_3 by impregnation method. The amount of deposited onto Al_2O_3 gold and silver nanoparticles was extremely low and in the range of 0.06-0.1%. SEM and TEM results show that the average size of gold nanoparticles attached to the surface of Al_2O_3 is varied from 10 to 25 nm. The catalytic activity of Al_2O_3/AuNPs-PVP nanocatalysts increases exponentially with induction period of time in dependence of molecular weight of PVP. It is shown that AgNPs have much lower catalytic activity than that of AuNPs.

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