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Preparation, Characterization and Catalytic Activity of Gold Nanoparticles Stabilized by Hydrophilic Polymers

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Optical properties, structure, size and morphology of colloidal gold nanoparticles (AuNPs) stabilized by a series of hydrophilic polymers possessing nonionic, anionic, cationic and amphoteric nature were characterized by visible spectroscopy, dynamic light scattering (DLS), X-ray diffraction (XRD) and scanning electron microscopy (SEM), transmission electron microscopy (TEM). The polymer-protected AuNPs were prepared by "one-pot" synthetic protocol. The kinetics of formation of AuNPs was determined. The influence of the molecular weight (M_w) of polymers and concentration of AuNPs on the size of AuNPs was shown. The catalytic activity of polymer-protected AuNPs with respect to hydrogenation of 4-nitrophenol was studied. High conversion degree of 4-nitrophenol to 4-aminophenol was evaluated by visible spectroscopy.

Keywords: Gold Nanoparticles, Hydrophilic Polymers, One-Pot Synthesis, Structure, Morphology, Catalysis.

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1. INTRODUCTION

The AuNPs attract considerable attention of researchers because of their unique optical, electrical, catalytic and other properties. A lot of polymers possessing nonionic, anionic, cationic and amphoteric nature are widely used as AuNPs protecting agents [1]. Various functionalized polymers as stabilizers to design "metal core – organic shell" hybrid nanoparticles architectures were reviewed in [2]. Several water-soluble polymers and random copolymers have been investigated for their ability to stabilize such AuNPs [3].

Catalysis is a central concept in chemistry, playing for instance, a key role in biological and industrial processes. Platinum, palladium, iridium, copper, silver and other noble metals are highly active, promoting many different types of organic reactions including hydrogenation, oxidation, and C – C bond formation, etc. In contrast to the high catalytic activity of Pt (Z = 78) or Ir (Z = 77), Au (Z =7 9) can also exhibit a high catalytic activity [4].

The present communication considers the results on synthesis, characterization and catalytic behavior of gold nanoparticles stabilized by hydrophilic polymers.

2. EXPERIMENTAL PART

2.1 Materials

Nonionic polymers such as poly(ethyleneglycol) (PEG), poly(N-vinylpyrrolidone) (PVP), anionic polymers – poly(acrylic acid) (PAA), gellan, cationic polymers – poly(ethyleneimine) (PEI), poly(N-vinylbenzyl-N,N,N-trimethylammonium chloride (PVBTMAC), poly(N,N-dimethyl-N,N-diallylammonium chloride) (PDMDAAC), JR-400 as well as amphoteric polymers – (co)polymers of N,N-dimethylaminoethylmethacrylate-methacrylic acid (DMAEM-MAA), and poly[N,N-diallyl-N-octadecylamine-alt-(maleic acid)] (PDAODMA) were purchased from Aldrich and Sigma (USA).

Potassium chloraurate 99%, 4-nitrophenol were commercial analytical grade substances ordered from Aldrich and used without further purification.

2.2 Methods

To characterize the physico-chemical and catalytic properties of polymer-protected gold nanoparticles and to identify products of hydrogenation of organic substrates UV-Vis spectroscopy, X-ray diffraction (XRD), Transmission electron microscope (TEM), Nuclear magnetic resonance (NMR), Gas chromatography-mass spectrometry (GC-MS), Gas chromatography, Dynamic light scattering(DLS) were used.

2.3 Preparation of AuNPs

The AuNPs stabilized by hydrophilic polymers were prepared by so-called "one-pot" method. For this V=5 mL, C=0.4% aqueous solution of polymer was mixed with 5 mL, 4% of potassium chloraurate and 4 mL 0.5M potassium hydroxide. After thoroughly mixing and heating of this mixture at 100 ^{0}C during several minutes the color of solution changed into dark-red (Fig. 1). In this process hydrophilic polymers act as reducing and stabilizing agents simultaneously.

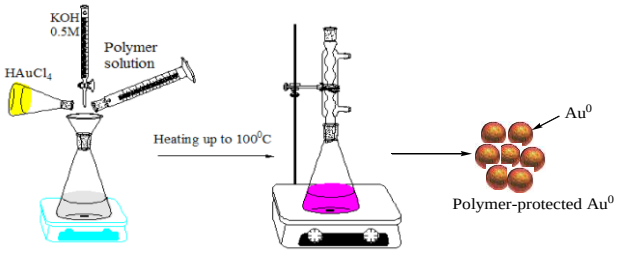

Fig. 1 – Preparation of AuNPs by "one-pot" synthetic protocol

Fig. 2 – Samples of AuNPs prepared by "one-pot" method

3. RESULTS AND DISCUSSION

3.1 Spectral Characteristics of AuNPs

The UV-Vis spectra of AuNPs stabilized by nonionic, anionic, cationic and amphoteric polymers are shown in Fig.3.

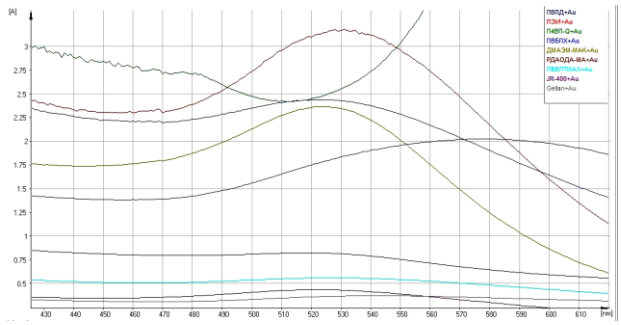

Fig. 3 – UV-Vis spectra of AuNPs stabilized by PVP, PEI, PVBTMAC, JR-400, DMAEM-MAA, PDAODMA

It is seen that the maximal absorbance of AuNPs for the most polymers is observed in the range of 520-530 nm. Table 1 shows the dependence of diameter of AuNPs on molecular weight (M_w) of used polymers. Size of AuNPs in dependence of the molecular weight of polymers is changed in the following order: PVP (3500) > PVP (10 000) > PVP (30 000) > PDMDAAC (200 000-350 000.

Table 1 – Molecular weight dependence of AuNPs diameters

Polymers	$M_w \cdot 10^{-3}$	Size of AuNPs, nm
PDMDAAC	200	3.0
PVP	30	3.3-4.4
	10	50.3-70.1
	3.5	28-100

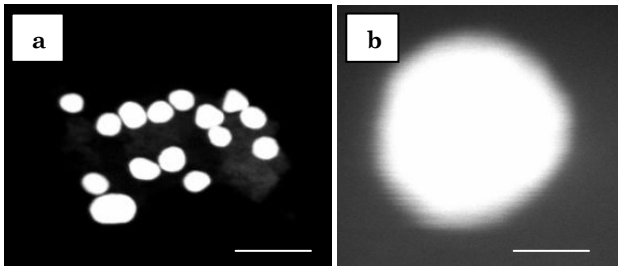

Fig. 4 – TEM pictures of AuNPs protected by PVP with M_w = 10 000 (a) and PDMDAAC with M_w = 200 000 (b). Scales are 50 (a) and 5 nm (b)

These results are in good agreement with TEM data (Fig. 4). The diameters of polymer-AuNPs are in the range of 10-40 nm.

Influence of PVP and $KAuCl_4$ concentrations on spectral characteristics of AuNPs was evaluated (Figs. 5 and 6). It is seen that the amount of AuNPs increases with increasing of both PVP and and $KAuCl_4$ concentrations.

The kinetics of AuNPs formation in the presence of PEI was studied. As seen from Figure 7 absorption spectra of AuNPs increases with time indicating on accumulation of gold nanoparticles with heating time.

Figure 8 shows that formation of AuNPs in the presence of PEI is completed during 170 sec while in the presence of JR-400 during 400 sec.

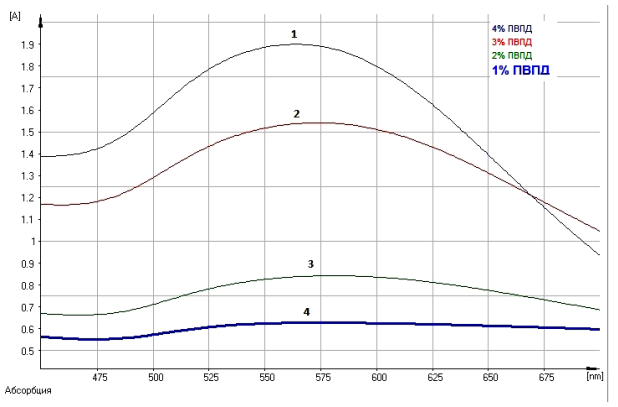

Fig. 5 – Influence PVP concentration on AuNPs formation. $[KAuCl_4] = 100\ mg \cdot L^{-1}$

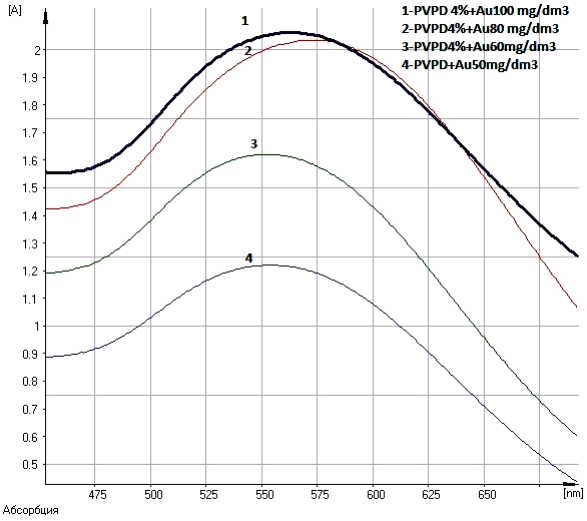

Fig. 6 – Influence $KAuCl_4$ concentration on AuNPs formation. [PVP] = 4 wt.%

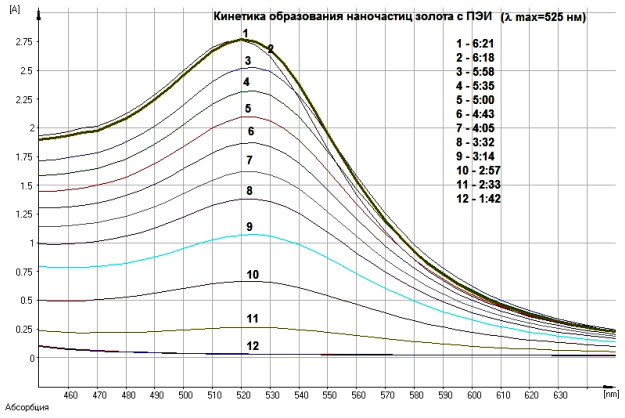

Fig. 7 – Accumulation of AuNPs in the presence of PEI

3.2 Hydrogenation of 4-nitrophenol by AuNPs

The catalytic reduction of 4-nitrophenol (4-NP) was studied in the standard quartz cuvette with 1 cm path length. By a series of experiments the optimal parameters of reaction were chosen: the ratio of $V_{4\text{-nitrophenol}}$:V_{NaBH4} = 1:1, $V_{polymer\text{-}AuNPs}$= 0.1 mL, 3 mL, $C_{4\text{-nitrophenol}}$ is 4 mmol/L and 3 mL, 0.5M $NaBH_4$ were mixed in a cuvette, then 0.1 mL of catalyst added, after

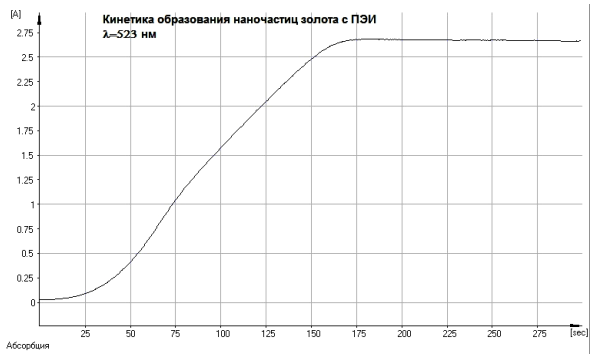

Fig. 8 – Time dependent changing of absorption spectra of AuNPs in the presence of PEI

the hydrogenation of 4-nitrophenol begun. The $NaBH_4$ at room temperature reacts with water, which leads to losing the activity of sodium borohydride in hydrogenation processes. Therefore hydrogenation reaction was carried out with fresh prepared ice-cold water solution of the $NaBH_4$. By methods of visible UV-spectroscopy, ^{1}H-NMR, GC analysis the kinetics and conversion of

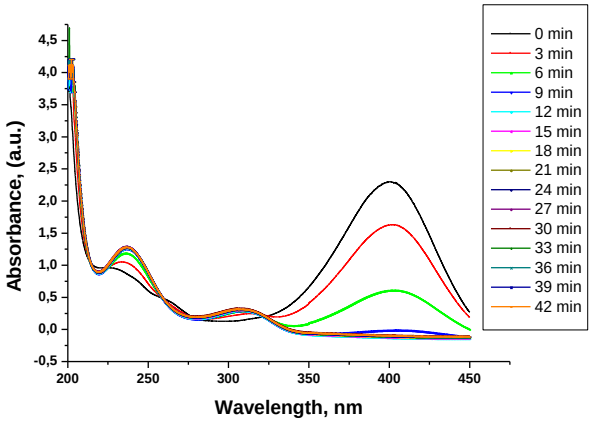

Fig. 9 – Kinetcis of hydrogenation of 4-nitrophenol by PDMDAAC-AuNPs

Table 2 – Hydrogenation of 4-NP

Catalyst	Time, min	Conversion, %
PVP-AuNPs	15-20	97
PDMDAAC-AuNPs	15-20	99

the reaction were evaluated. Figure 9 shows the catalytic hydrogenation of 4-NP by PDMDAAC-stabilized AuNPs. It clearly seen that with increasing of 4-aminophenol (4-AP) content, the absorption peak at 310 nm becomes more intensive, while the absorption peak of 4-nitrophenol at 420 nm disappears with time. As seen from Table 2, polymer-AuNPs is effective catalysts that convert 4-nitrophenol to 4-aminophenol during 15-20 min with high yield. Accumulation of aminophenol in the course of hydrogenation of 4-AP is confirmed by ^{1}H NMR data. In ^{1}H NMR spectra of 4-nitrophenol the following groups were identified: δ = 11.04 (s, OH-), 8.09-8.13 (m, *o*-phenyl), 6.90-6.95 (m, *m*-phenyl-) while ^{1}H NMR spectra of 4-aminophenol exhibited the following functional groups: δ = 8.35 (s, 2H, NH_2), 6.40-6.51 (m, 4H, phenyl-), 4.39 (1H, OH-). Appearance of intensive peak at δ = 8.35 that is characteristic for NH_2 groups confirms the formation of 4-AP in the course of hydrogenation of 4-NP.

4. CONCLUSIONS

Properties of gold nanoparticles obtained by "one-pot" method were analyzed by UV-Vis-spectroscopy, NMR, TEM, GC, DLS methods. It was found that increasing of the molecular weight of PVP leads to decreasing of the size of AuNPs. Catalytic properties of AuNPs were investigated in hydrogenation of 4-nitrophenol. It was shown that AuNPs during 15-20 min converts 4-NP to 4-AP up to 97-99%.

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