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Preparation, characterization and catalytic activity of gold nanoparticles stabilized by poly (n-vinylpyrrolidone) and poly (N,N-dimethyl-N,N-diallylammonium chloride)

Abstract. Optical properties, structure and morphology of colloidal gold nanoparticles (AuNPs) stabilized by poly (N-vinylpyrrolidone) (PVP) and poly(N,N-dimethyl-N,N-diallylammonium chloride) (PDMDAAC) were characterized by visible spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The influence of the molecular weight (M_w) of PVP on the size of AuNPs was studied. The catalytic activity of polymer-protected AuNPs with respect to hydrogenation of *p*-nitrophenol was studied. High conversion degree of 4-nitrophenol to 4-aminophenol was found.
***Keywords*:** colloidal gold nanoparticles, optical properties, structure, morphology.

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=79) 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 PVP and PDMDAAC.

Experimental Part

Materials. Potassium chloraurate 99%, PDMDAAC 20 % aqueous solution, PVP with various M_w, *p*-nitrophenol were commercial analytical grade, ordered from Aldrich and used without further purification.

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) measurements, Nuclear magnetic resonance (NMR), Gas chromatography-mass spectrometry (GC-MS), Gas chromatography, Dynamic light scattering(DLS) were used.

Results and Discussion

Preparation of polymer-protected AuNPs. The AuNPs stabilized by PVP and PDMDAAC were prepared by so-called "one-pot" method. For this

V=5 mL, C=0.4% aqueous solution of PVP (or PDMDAAC) 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.

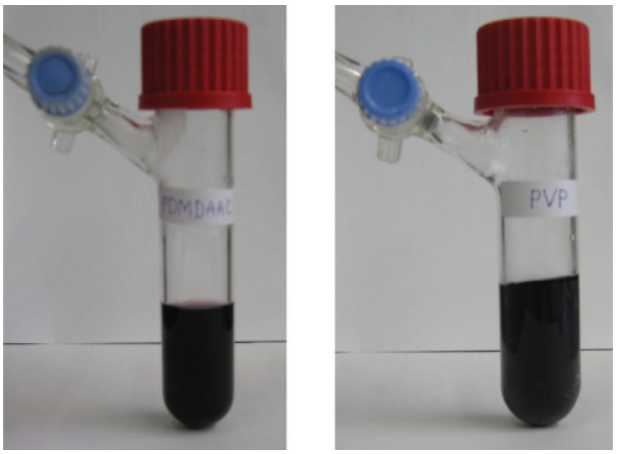

Figure 1 – AuNPs stabilized by PVP and PDMDAAC

Figures 2, 3 show the UV-Vis spectra of AuNPs protected by PVP and PDMDAAC. It is seen that the maximal absorbance is observed at 530 nm and 540 nm for PVP-AuNPs and PDMDAAC-AuNPs respectively.

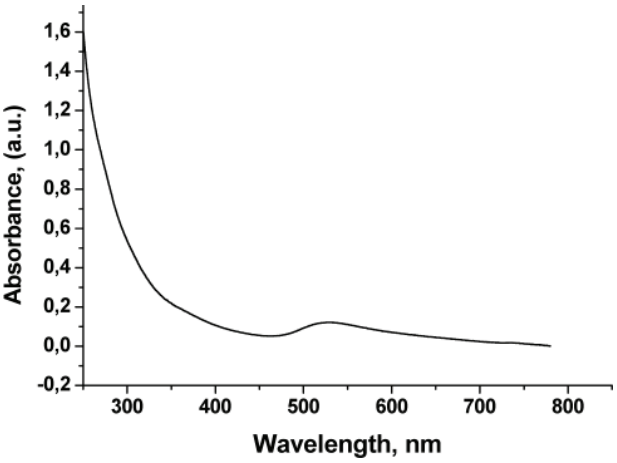

Figure 2 –UV-Vis spectra of AuNPs stabilized by PVP

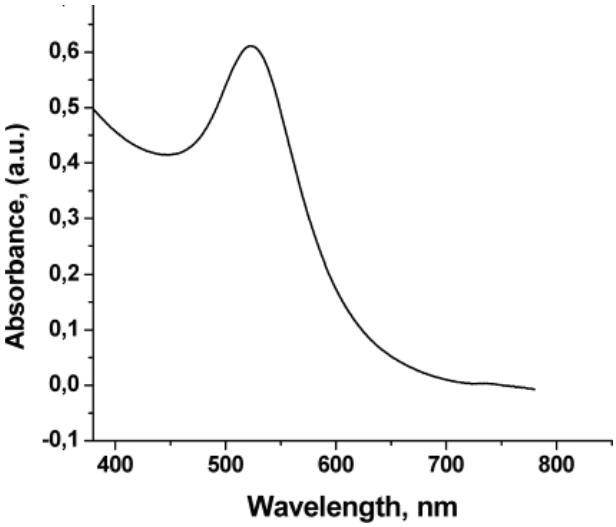

Figure 3 – UV-Vis spectra of AuNPs stabilized by PDMDAAC

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)-AuNPs > PVP(10 000)-AuNPs > PVP(30 000)-AuNPs > PDMDAAC (200 000-350 000)-AuNPs.

Table 1 – Results of DLS-measurement.

M_w of polymers	Size of AuNPs, nm
PDMDAAC 200 000-350 000	3.0
PVP 30 000	3.3-4.4
PVP 10 000	50.3-70.1
PVP 3 500	28-100

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

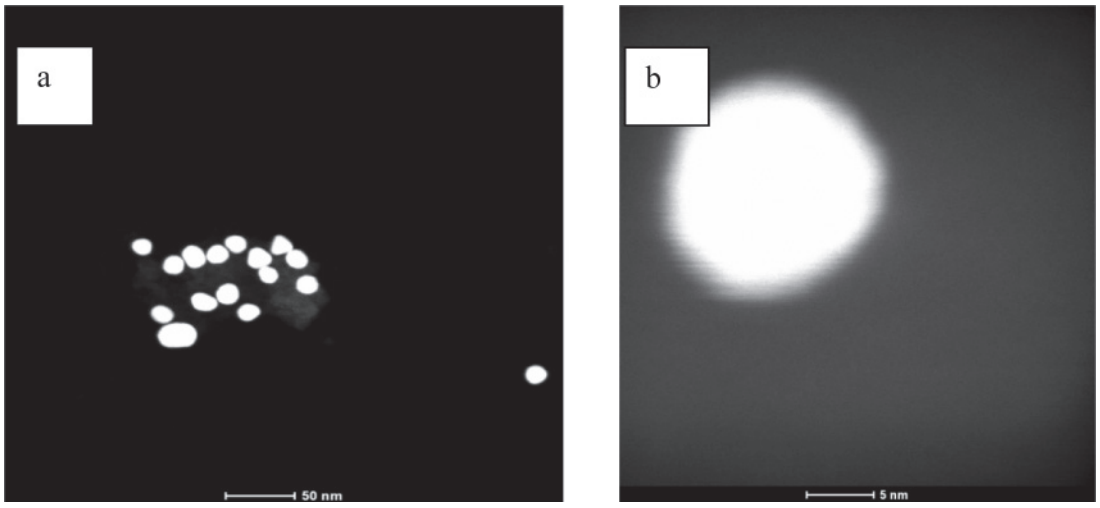

Figure 4 – TEM pictures of AuNPs protected by PVP 10 000 (a) and PDMDAAC (b)

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 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 the reaction were evaluated.

Figure 5 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.

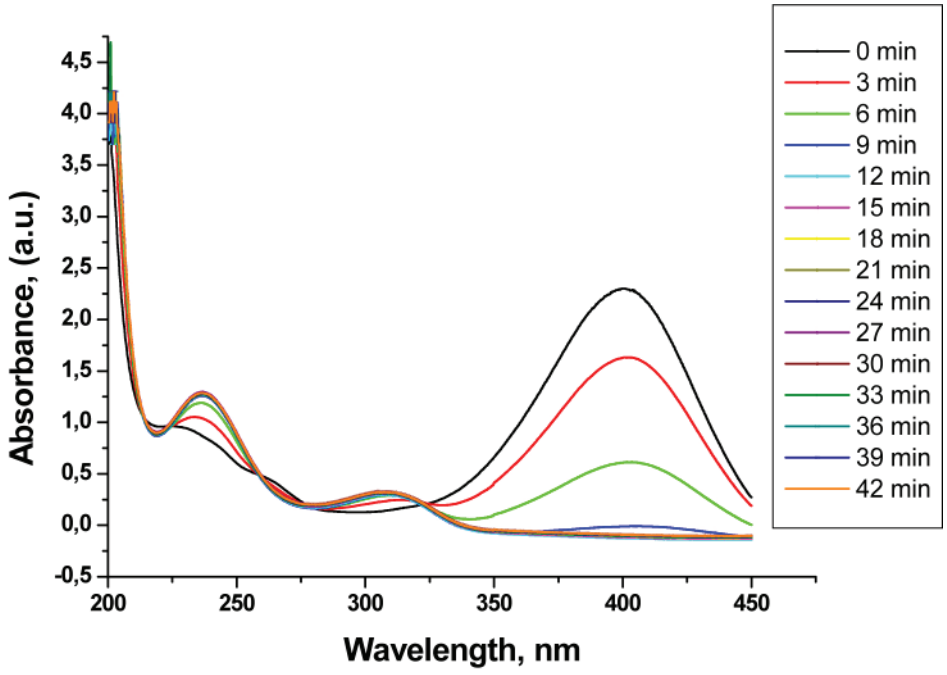

Figure 5 – Kinetcis of hydrogenation of 4-nitrophenol by PDMDAAC-AuNPs

Table 2 – Hydrogenation of 4-NP

Substrate	Catalyst	Reducing agent	Time, min	Conversion, %
4-NP	PVP-AuNPs	$NaBH_4$	15-20	97
4-NP	PDMDAAC-AuNPs	$NaBH_4$	15-20	99

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 (Figs. 6). 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.

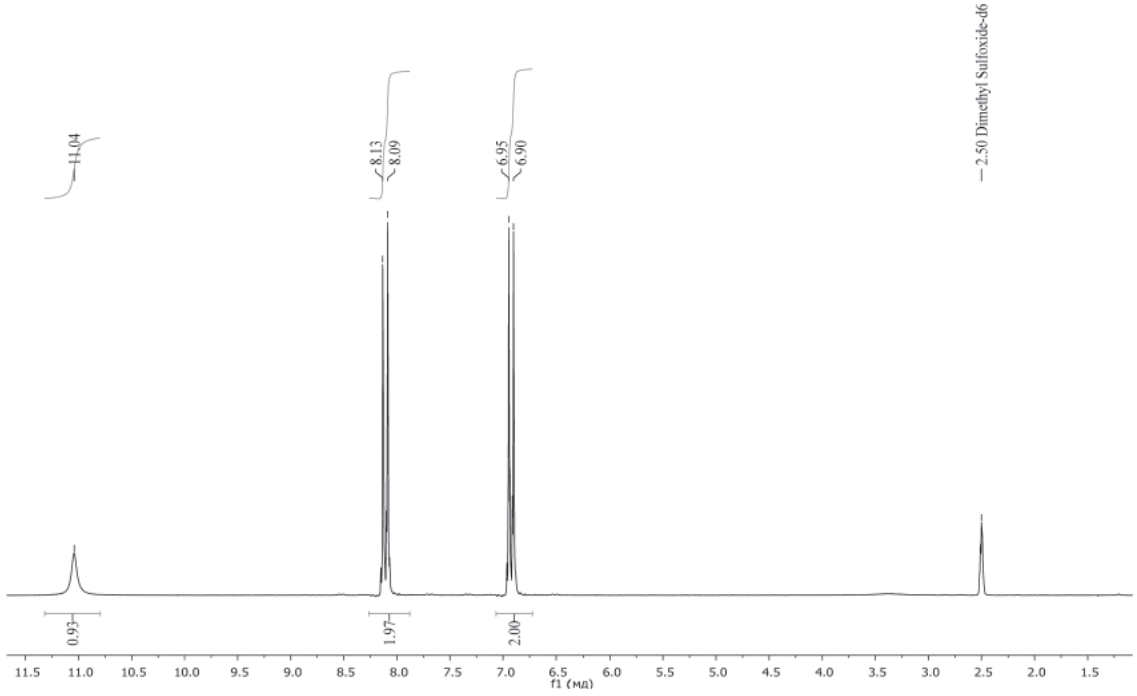

Figure 6 – ^{1}H NMR spectra of 4-nitrophenol (DMSO-d6, T = 298 K, 1H: 200.130 MHz)

Conclusion

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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Поливинилпирролидон және полидиметилдиаллиламоний хлорид полимерлерімен тұрақтандырылған алтын нанобөлшектерінің синтезі, қасиеттері мен каталитикалық белсендігі

Мақалада поли(N-винилпирролидон)және поли(N,N-диметил-N,N-диаллиламмоний хлорид) арқылы тұрақтандырылған алтын нанобөлшектерінің синтезі, зерттелуі және каталитикалық белсенділігі қарастырылған. Полимерлермен тұрақтандырылған алтын нанобөлшектерінің (полимер-АНБ) су ертіндісіндегі қасиеттері УК-көрініс спектроскопия, динамикалық лазерлі сәуле тарау, ЯМР спектроскопиясы, ал қатты түрде ретгендифрактометр және шағылу электронды микроскопия әдістерімен зерттелген. Полимер-АНБ қатысуымен 4-нитрофенолды гидрлеу өнімдері хроматомасс спектроскопиясы, газ хроматографиясы және ЯМР спектроскопиясымен анықталған.

Түйін сөздер: коллоидты алтын нанобөлшектер, оптикалық қасиеттер, құрылым, морфология.

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Синтез, свойства и каталитическая активность наночастиц золота, стабилизированных поливинилпирролидоном и полидиметилдиаллиламония хлоридом

В статье описывается синтез, исследование и каталитическая активность наночастиц золота, стабилизированных поли(N-винилпирролидоном) и поли(N,N-диметил-N,N-диаллиламмоний хлоридом). Свойства полимер-протектированных наночастиц золота (полимер-НЧЗ) в водном растворе изучены методами УФ-видимой спектроскопии, динамического лазерного светорассеяния, ЯМР спектроскопии, а в твердом состоянии – методами рентгенодифрактометрии и просвечивающей электронной микроскопии. Продукты гидрирования 4-нитрофенола с участием полимер-НЧЗ идентифицированы методами хроматомасс спектроскопии, газовой хроматографии и ЯМР спектроскопии.

Ключевые слова: коллоидные наночастицы золота, оптические свойства, структура, морфология.