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### Catalytic activity of poly(N-vinylpyrrolidone) protected gold nanoparticles deposited on ZnO

**Abstract.** Gold (AuNPs) nanoparticles protected by poly(N-vinylpyrrolidone) (PVP) were prepared by «one-pot» synthetic protocol. Absorption spectra, size, morphology, structure and thermal properties of AuNPs were studied by UV-Vis spectroscopy, DLS, TEM and SAXS. According to DLS and SAXS measurement the average size of AuNPs stabilized by PVP in aqueous solution is varied from 6 to 15 nm. PVP protected AuNPs were deposited on zinc oxide by impregnation method. TEM images reveal that the average size of AuNPs-PVP deposited on the surface of ZnO is arranged between 6 and 10 nm and coincides well with DLS and SAXS measurements. The catalytic activity of polymer-protected AuNPs supported on the surface of ZnO was evaluated with respect to decomposition of hydrogen peroxide. The optimal conditions H<sub>2</sub>O<sub>2</sub> decomposition in dependence of catalysts amount, concentration of substrate and temperature was found.

**Key words:** Gold nanoparticles, hydrophilic polymers, zinc oxide, catalysis, hydrogen peroxide decomposition.

#### Introduction

Over the past few years, gold nanoparticles (AuNPs) due to their unique properties such as optical, mechanical, electrical and catalytic activity play crucial role for industries [1-3]. Catalytic activity of AuNPs is well known since 1980's when the pioneering work of Haruta has been published [4]. Catalysts based on AuNPs and supported on metal oxides have attracted researcher's attention because of their high catalytic activity for various oxidation and reduction reactions under mild conditions [5].

Many methods such as co-precipitation [6], colloidal deposition, laser vaporization, chemical vapor deposition (CVD), organic gold-complex grafting, deposition precipitation (DP), impregnation [7], liquid phase grafting, cation exchange and amorphous metal alloy methods have been used to prepare high-activity gold catalysts. Some of them

involve many sophisticated apparatuses and a number of processing steps. Thus, in order to acquire efficient gold catalysts, novel preparation routes for obtaining finely gold on metal oxides have recently been widely investigated.

In the present communication we stabilized AuNPs with poly(N-vinylpyrrolidone), determined their sizes, prepared aqueous solutions of AuNPs, immobilized them on zinc oxide by impregnation method and studied the catalytic activity for decomposition of H<sub>2</sub>O<sub>2</sub> and to determine its optimal conditions.

#### Materials and methods

Standard aqueous solution of tetrachlorauric acid HAuCl<sub>4</sub> with concentration 100 mg·L<sup>-1</sup> was purchased from Sigma-Aldrich. As polymeric stabilizing agents – poly(N-vinylpyrrolidone) (PVP) with Mn= 10 kD, as inorganic supporter – zinc ox-

ide purchased also from Sigma-Aldrich were used without further purification.

Absorption spectra of AuNPs 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). Transmission electron microscope (TEM) measurement was carried out with on JEM-1011 (JEOL, Japan), size of the synthesized nanoparticles was performed on small angle X-ray scattering equipment HECUS S3-micro (Austria).

AuNPs stabilized by PVP were obtained by «one-pot» synthetic protocol [8]. For instance, aqueous solutions of HAuCl<sub>4</sub> (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.

PVP-AuNPs were supported on ZnO by impregnation method. For this 0.2 g of ZnO was added to 5 mL (0,25wt.%) of PVP-AuNPs and stirred during 5 hours. The precipitate was separated by preparative centrifuge «Eppendorf 5810R» (Germany) at 10·103 rpm, then it was washed out 5 times with distilled water. The precipitate was dried in vacuum oven at 50 °C. The powders ZnO with supported PVP-AuNPs /ZnO were used as catalysts for decomposition of H<sub>2</sub>O<sub>2</sub>.

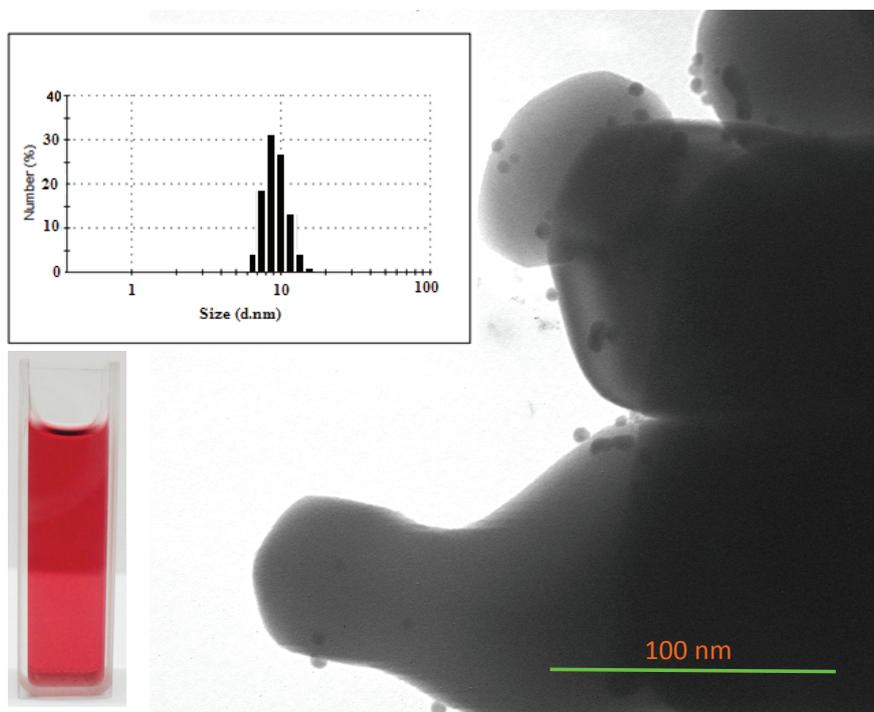
### 3. Results and their discussion

The size of synthesized nanoparticles of gold stabilized by PVP with Mw=10 000 were carried out by dynamic light scattering device, and the size of nanoparticles deposited on zinc oxide was performed by SAXS equipment. TEM image corresponding to AuNPs deposited on zinc oxide showed that average size of the nanoparticles is 8.2±0.8 nm (see Fig.1) which is in good agreement with DLS and SAXS results ( $r = 4.7$  nm). From the SAXS-measurements the radius of nanoparticles has been calculated by Guinier formula (Eq. 1, 2) and with the help of the SAX-scattering curve (Fig.2).

$$I(h) = I(0) \cdot \exp(-Rg^2 \cdot h^2/3) \quad (1)$$

$$Rg^2 = 3 \cdot R^2/5 \quad (2)$$

Decomposition of H<sub>2</sub>O<sub>2</sub> was carried out in thermostated glass reactor equipped by magnetic stirrer. Thin powders of polymer protected and supported on metal oxides nanocatalysts ZnO/PVP-AuNPs were dispersed in 1 mL aqueous solution of H<sub>2</sub>O<sub>2</sub> and the volume of released oxygen was fixed by burette for measuring the volume of gases at definite time interval.



**Figure 1** – TEM image and size distribution of PVP 10 000/AuNPs supported on ZnO

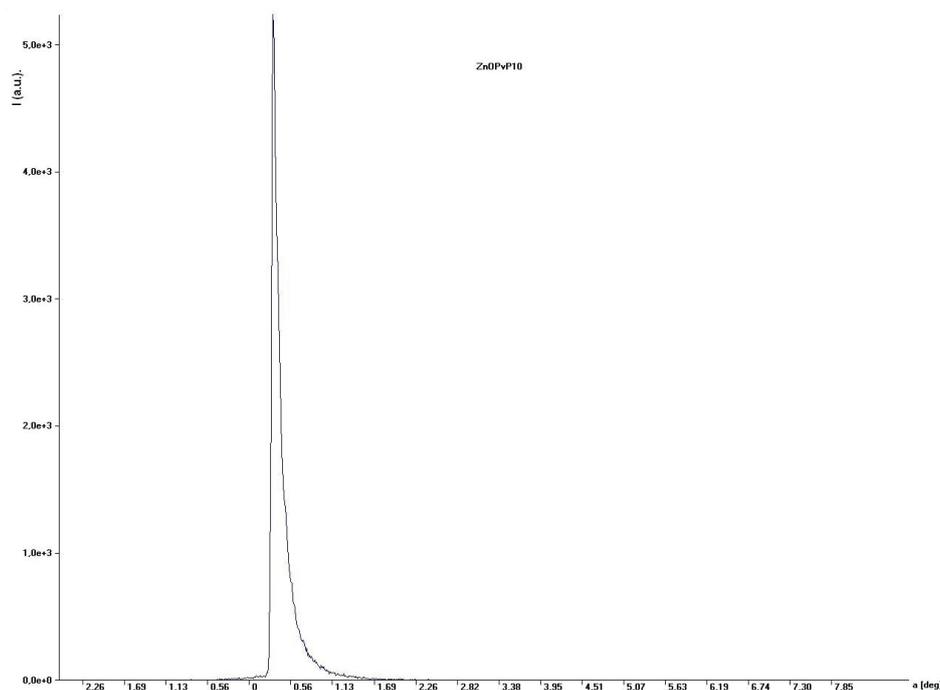


Figure 2 – SAXS curve of PVP/AuNPs/ZnO

The influence of catalyst amount ( $m_{\text{cat}}$ ), concentration of substrate ( $[\text{H}_2\text{O}_2]$ ) and temperature ( $T$ ) was studied in order to find the optimal conditions of  $\text{H}_2\text{O}_2$  decomposition. At concentration of  $[\text{H}_2\text{O}_2] = 30$  wt.% and  $T = 318\text{K}$  the decomposition rate of

hydrogen peroxide increases with increasing of the  $m_{\text{cat}}$  (Fig.11). As seen from Fig. 3 the rate of decomposition of  $\text{H}_2\text{O}_2$  at  $m_{\text{cat}} = 30$  mg is higher than at  $m_{\text{cat}} = 50$  mg. Thus the optimal amount of catalyst for  $\text{H}_2\text{O}_2$  decomposition is 30 mg.

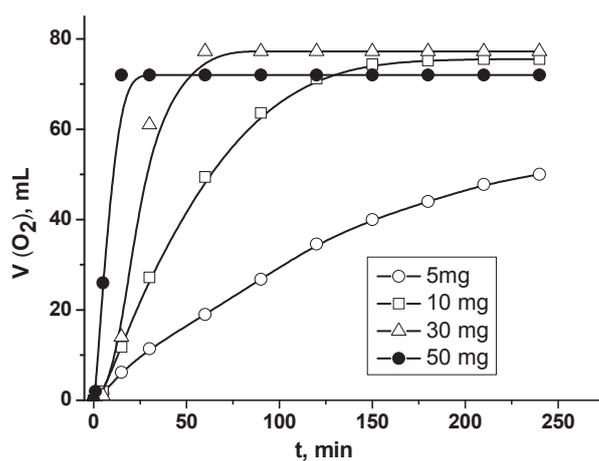
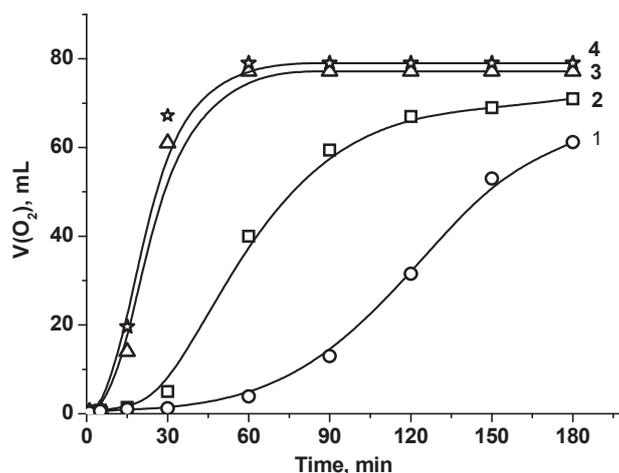


Figure 3 – Decomposition rate of hydrogen peroxide in dependence of the  $m_{\text{cat}}$  on ZnO/AuNPs-PVP-10 kD.  $T = 318\text{K}$ ,  $[\text{H}_2\text{O}_2] = 30$  wt.%.



**Figure 4** – Decomposition of hydrogen peroxide in the presence of ZnO/AuNPs-PVP-10 kD at different temperatures. T = 298 (1), 308(2), 318(3), and 328 K (4).  $m_{\text{cat}} = 30$  mg,  $[\text{H}_2\text{O}_2] = 30$  wt.%

At  $m_{\text{cat}} = 30$  mg, the decomposition rate of hydrogen peroxide gradually increases with increasing of temperature (Fig.4). However the rate of  $\text{H}_2\text{O}_2$  decomposition at and T = 328 is very close to  $T = 318$  K that is optimal temperature.

#### Conclusion

Poly(N-vinylpyrrolidone) protected gold nanoparticles were prepared by «one-pot» method and impregnated on the surface of ZnO. The average size of AuNPs stabilized by PVP is varied from 6 to 10 nm. The catalytic activity of ZnO/AuNPs-PVP nanocatalysts increases exponentially with induction period of time in dependence of molecular weight of PVP.

The optimal conditions of  $\text{H}_2\text{O}_2$  decomposition were the following: the amount of catalyst is  $m_{\text{cat}} = 30$  mg, the substrate concentration is  $[\text{H}_2\text{O}_2] = 30$  wt.% and T = 318 K.

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