

## Catalytic Properties of Gel-Immobilized Gold Nanoparticles in Decomposition of Hydrogen Peroxide

Elmira K. Nurgaziyeva<sup>1,2</sup>, Gulnur S. Tatykhanova<sup>1,3</sup>, Grigoriy A. Mun<sup>2</sup>,  
Vitaliy V. Khutoryanskiy<sup>4</sup>, Sarkyt E. Kudaibergenov<sup>1,3</sup>

<sup>1</sup> *Laboratory of Engineering Profile, K.I. Satpayev Kazakh National Technical University, Almaty, Kazakhstan*

<sup>2</sup> *al-Farabi Kazakh National University, Almaty, Kazakhstan*

<sup>3</sup> *Institute of Polymer Materials and Technology, Almaty, Kazakhstan*

<sup>4</sup> *Reading School of Pharmacy, University of Reading, Whiteknights, Reading, UK*

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This paper reports the study of hydrogen peroxide decomposition catalyzed by polymer-protected gold nanoparticles (AuNPs) immobilized within polyacrylamide hydrogel. The stabilization of AuNPs was achieved using hydrophilic polymers. Embedding of AuNPs stabilized with various polymers into polyacrylamide hydrogels was carried out using three ways: "in situ" polymerization, sorption and borohydride methods. Size, shape and morphology of AuNPs were characterized by various physicochemical methods.

**Keywords:** Gold nanoparticles, Hydrogels, Hydrophilic Polymers, Stabilization, Catalysis.

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### 1. INTRODUCTION

Hydrogels have found numerous applications due to their unique properties such as high water content, softness, flexibility, biocompatibility and ease of synthesis. Their resemblance to living tissue opens up many opportunities for applications in biomedical areas. Nowadays, hydrogels are used for manufacturing contact lenses, hygiene products, tissue engineering scaffolds, drug delivery systems and wound dressings [1, 2].

This paper reports the study of hydrogen peroxide decomposition catalyzed by polymer-protected gold nanoparticles (AuNPs) immobilized within polyacrylamide hydrogel (PAAH).

### 2. EXPERIMENTAL PART

#### 2.1 Materials

Poly-N-vinylpyrrolidone (PVP, MW 40 kDa), branched polyethylenimine (PEI, MW 25 kDa) and NaOH were purchased from Sigma – Aldrich (USA). HAuCl<sub>4</sub> was purchased from Altey (Kazakhstan). NaBH<sub>4</sub> was purchased from AppliChem (Germany). All chemicals were used without further purification.

#### 2.2 Synthesis of AuNPs

AuNPs were synthesised by mixing 4 mL 0.5M KOH with 5 mL 4 w/v % PVP or 5 mL 4 w/v % PEI, then addition of 5 mL of 100 mg/L HAuCl<sub>4</sub> solution into the mixture and heating it at 100°C for several minutes until the solution turned red, which indicates the formation of gold nanoparticles. The synthesized gold nanoparticles were purified by dialysis against 4 L deionized water for 48 hours using cellulose membranes (molecular weight cut off 12-14 kDa, Medicell International Ltd, UK). Water was changed every 2 hours. Aqueous dispersions of gold nanoparticles were stored in a dark place at room temperature.

#### 2.3 Immobilization of AuNPs into PAAm matrix

The immobilization of AuNPs into polyacrylamide hydrogel was carried out by 3 ways:

gel-immobilized AuNPs were prepared by polymerizing the mixture of 500 mg acrylamide dissolved in 5 mL PEI- or PVP-protected AuNPs aqueous dispersions in the presence of 10 mg methylene bisacrylamide as a crosslinking agent and 10 mg ammonium persulfate as an initiator. The reaction mixture was purged with argon for 5 min; then it was kept at 60°C. The hydrogels were formed within 30 min of the reaction and then they were washed in distilled water for 3-4 days to get rid of unreacted monomers. The purified hydrogel samples were crushed and dried in air to a constant mass;

##### 1) Sorption method:

Pure polyacrylamide hydrogels were synthesized using three-dimensional polymerization of 500 mg acrylamide in 5 mL water in the presence of 10 mg of methylene bisacrylamide and 10 mg of ammonium persulphate. This solution mixture was held at 60 °C for 30 min to form hydrogels. These hydrogels were purified as described above. Then these materials were air dried and 1 g of dry sample was immersed in 10 mL AuNPs aqueous dispersion for 24 hours. After washing and grinding, the hydrogels were dried to a constant mass. The sorption of AuNPs by dry hydrogels resulted in coloured samples, which were subsequently dried in air.

##### 2) Borohydride method:

The preparation of AuNPs immobilized hydrogels in this method was carried out by immersing dried hydrogel samples into 100 mg/L solution of HAuCl<sub>4</sub> for 24 hours. After sorption the hydrogel samples were placed into 5 mL 0.1 M solution of sodium borohydride for 20 min, which resulted in colored samples indicating the formation of AuNPs. These hydrogels were cut into smaller pieces and dried in air to a constant mass.

## 2.4 Dynamic Light Scattering

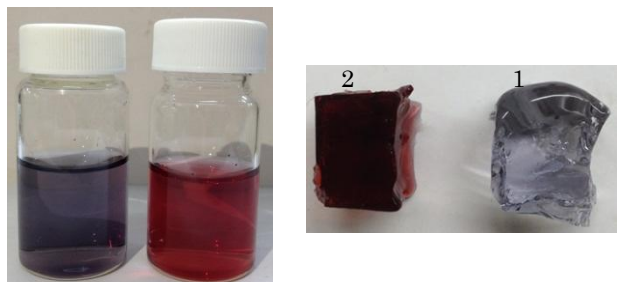
Particle size distributions and zeta-potential of gold nanoparticles (AuNPs) in aqueous dispersions were measured using dynamic light scattering (DLS, Malvern Zetasizer Nano ZS 90, UK).

## 2.5 Transmission electron microscopy (TEM)

Transmission electron microscopy images of gold nanoparticles in aqueous dispersions and in gels were recorded using JEM-1011 (Japan) at an accelerating voltage of 80 kV. The samples for investigation were applied as a dispersion of AuNPs dripped onto standard copper grid with subsequent drying in air. Gel samples were micronized and a drop of microgel aqueous suspension was placed on TEM grid and air dried.

## 2.6 Decomposition of hydrogen peroxide

Decomposition of  $H_2O_2$  was carried out in a thermostated glass reactor equipped with a magnetic stirrer (Figure 1s, Supporting Information). The powdered catalyst (5 to 50 mg) was dispersed in 1 mL  $H_2O_2$ . The volume of released oxygen was determined using a gas-measuring burette at different time intervals. In different decomposition experiments, the concentration of  $H_2O_2$  was varied from 10 to 30 wt%, the temperature from 25 to 55°C and the catalyst mass from 5 to 50 mg.



**Fig. 1** – PVP (purple)- and PEI (red)-stabilized gold nanoparticles and gel-immobilized (1-PVP, 2-PEI) AuNPs

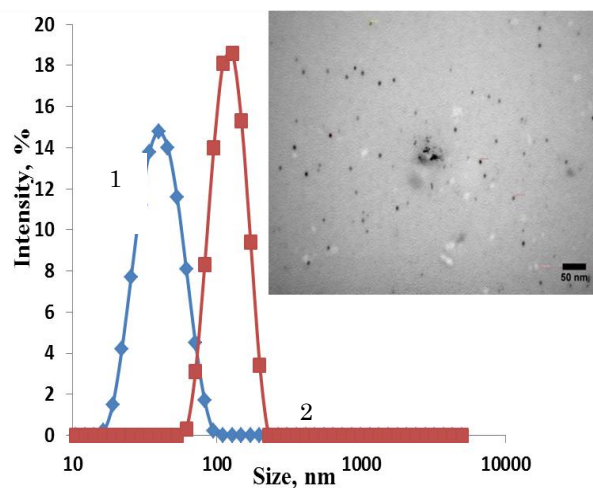
## 3. RESULTS AND DISCUSSION

### 3.1 UV-Vis spectroscopy of AuNPs solutions and hydrogels

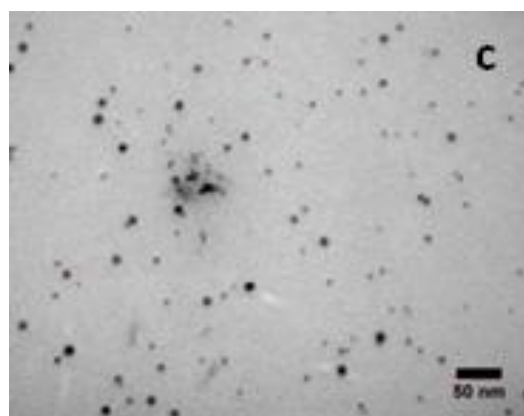
AuNPs were synthesized by reduction of  $HAuCl_4$  in aqueous solutions containing either 4 w/v % of PVP or 4 w/v % PEI under alkali conditions (achieved by addition of 4 mL 0.5M KOH to the reaction mixture). The reaction was initiated by increasing temperature up to 100 °C, which resulted in the aqueous mixtures becoming colored within a few minutes. The change of solution color indicated the formation of AuNPs sols. The synthesized nanoparticles were initially characterized using dynamic light scattering and TEM (Figure 2).

The use of different water-soluble polymers for reduction of  $HAuCl_4$  results in formation of nanoparticles substantially differing in their sizes as measured by dynamic light scattering: the hydrodynamic diameters are  $46 \pm 10$  nm and  $128 \pm 20$  nm for AuNPs synthesized in the presence of PVP and PEI, respectively. It is interesting to note that the comparison of DLS data with

TEM images of the nanoparticles reveals a significant difference in sizes. The analysis of TEM results using ImageJ software indicates that the nanoparticles formed in PEI have diameters of 8.170 nm. This dramatic discrepancy between DLS and TEM results is explained by different physical principles used by these two sizing techniques. DLS is a technique that measures light scattered by the objects present in solutions and will be able to detect individual macromolecules. AuNPs formed in the presence of water-soluble polymers have a core-shell structure with the core made of gold and a hydrophilic shell made of macromolecules of a water-soluble polymer. DLS measurements in this case will provide the size distribution for the nanoparticles together with a hydrated shell. TEM, on the contrary, is based on transmission of accelerated electrons through the sample and, in the absence of specific staining agents, this technique will be able to detect only dense objects such as gold-based core. The comparison of both DLS and TEM data allows establishing the structural features of AuNPs prepared in the presence of PVP and PEI.



**Fig. 2** – Size distributions of gold nanoparticles as measured by dynamic light scattering. AuNPs were synthesized in the presence of PVP (1) and PEI (2). Insert: Exemplary TEM image of AuNPs synthesized in the presence of PEI.



**Fig. 3** – Hydrogel samples with immobilized AuNPs, prepared using “in-situ” method. PVP (1) and PEI (2) were used for stabilization of nanoparticles. TEM image of PEI-protected AuNPs immobilized within a hydrogel using “in-situ” method (c).

Hydrogel immobilized gold nanoparticles were prepared using three approaches: (1) "in-situ" immobilization method; (2) sorption method; and (3) borohydride method. Figure 2 shows the images of selected hydrogel samples with immobilized AuNPs prepared using "in-situ" and sorption methods.

Table 1 presents the comparison of the dimensions and other physicochemical properties of AuNPs in aqueous dispersions and immobilized within hydrogels. Analysis of TEM images of AuNPs immobilized within a hydrogel indicates that the size of gold core has a diameter very similar to the sizes of the nanoparticles before their incorporation into the hydrogels. Zeta-potential measurements indicate that of AuNPs formed in the presence of PVP and PEI in aqueous dispersions have slightly negative values (-10.52 mV and -9.31 mV, respectively). Considering that these nanoparticles are very stable in dispersion, it could be concluded that their stabilization is related to the sterical effects caused by highly hydrated macromolecules forming their shell rather than their charge interactions.

**Table 1** – Physicochemical properties of AuNPs in dispersions and in hydrogels

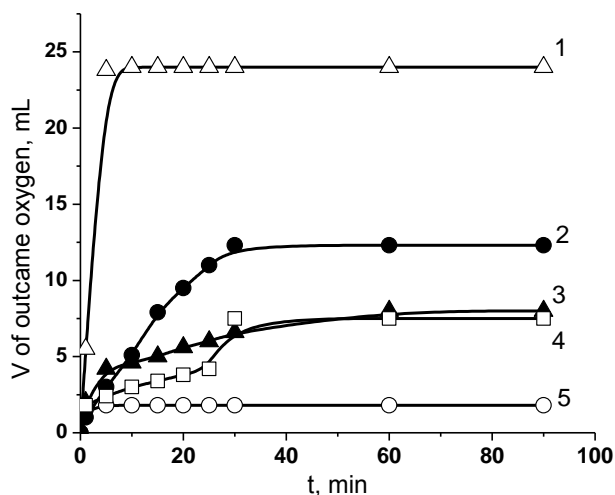
Samples	TEM, nm	DLS, nm	PDI	Zeta potential, mV
PEI-protected AuNPs (solution)	7.0±0.53	128±20	0.427	-9.31
PVP-protected AuNPs (solution)	*	46 ± 10	0.553	-10.52
PEI-protected AuNPs within a hydrogel	7.310±0.005	*	*	*
PVP-protected AuNPs within a hydrogel		*	*	*

\* - not measured.

### 3.2 Decomposition of hydrogen peroxide by AuNPs immobilized within polyacrylamide hydrogel

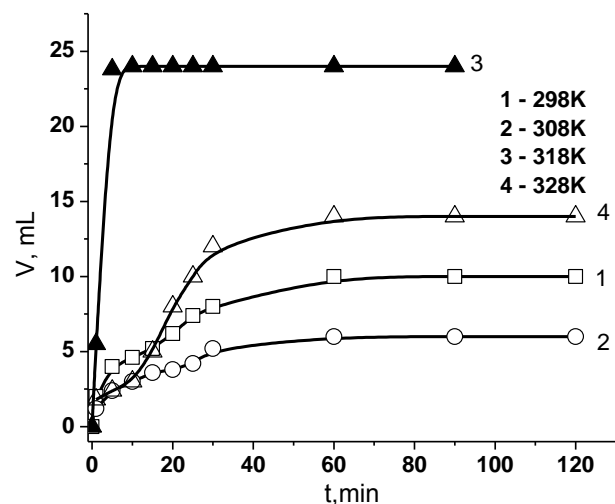
Gel immobilized gold nanoparticles as catalysts for decomposition of hydrogen peroxide. The kinetic curves of hydrogen peroxide decomposition in the presence of gel-immobilized AuNPs prepared using different methods are shown in Figure 4.

The catalytic activity of gel-immobilized gold nanoparticles in decomposition reaction of hydrogen peroxide is substantially dependent on the method of their preparation. The efficiency to catalyze this reaction is observed with the use of PEI-stabilized AuNPs immobilized into a hydrogel using sorption method. depending on the production method is changed as follows: Method 2 (stabilizer PEI) > method 2 (PVP stabilizer) > Method 2 ≈ Method 1 (stabilizer PEI) > Method 1 (stabilizer PDCA).



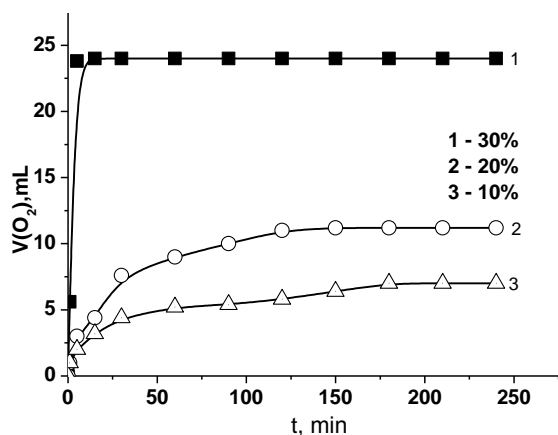
**Fig. 4** – Decomposition of hydrogen peroxide in presence of gel-immobilized AuNPs prepared using sorption method with PEI (1) and PVP (2) as stabilizing agents; borohydrate method (3) and "in-situ" method with PEI (4) and PVP (5) as stabilizing agents. Experimental conditions: 30 mg of a dry hydrogel powder were used in these experiments. Concentration of hydrogen peroxide was 30 wt % and all reactions were conducted at 45 °C.

Thus, the most active catalyst for hydrogen peroxide decomposition is PEI-protected and PEI-gel-immobilized AuNPs obtained by sorption method (2). In this regard, all further studies for finding optimal decomposition of hydrogen peroxide conditions in the presence of gel-immobilized AuNPs were performed with this catalyst. In particular, we studied the effect of weight of the catalyst, reaction temperature, substrate concentration on the kinetics of the decomposition of hydrogen peroxide. Figure 5 shows the results of the effect of temperature on the kinetics of hydrogen peroxide decomposition at a constant weight of catalyst 30 mg and a hydrogen peroxide concentration of 30%. Maximum number has consumed oxygen corresponds to 318K, which is the optimal decomposition temperature of the substrate.



**Fig. 5** – Decomposition of hydrogen peroxide in dependence on the temperature (Au-PEI/PAAH-sorption).  $m_{cat} = 30$  mg,  $C(H_2O_2) = 30\%$

Figure 6 shows the influence of the concentration of hydrogen peroxide on the kinetics of decomposition at the optimum temperature 318K and constant mass of catalyst 30 mg. In these experiments, the optimum concentration of the substrate is selected to be 30%.



**Fig. 6** – Decomposition of hydrogen peroxide depends on the concentration of hydrogen peroxide (Au / PEI-sorption): T = 318K,  $m_{\text{cat}} = 30$  mg

Thus, the optimal conditions decomposition of hydrogen peroxide in the presence of gel-immobilized gold nanoparticles are following: T = 318K, the mass of catalyst - 30 mg, substrate concentration - 30%.

#### 4. CONCLUSIONS

Gold nanoparticles stabilized by various hydrophilic polymers encapsulated within hydrogel matrix. The physic-chemical properties were investigated by DLS, TEM analyses. The catalytic properties of gel-immobilized AuNPs were studied in decomposition of H<sub>2</sub>O<sub>2</sub>.

#### REFERENCES

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