



Research Article

Impact of Testing Temperature on the Structure and Catalytic Properties of Au Nanotubes Composites

Anastassiya A. Mashentseva^{1*}, Maxim V. Zdorovets¹⁻³, Daryn B. Borgekov^{1,2}

¹The Institute of Nuclear Physics of the Republic of Kazakhstan, 050032, Ibragimov str., 1, Almaty, Kazakhstan

²L.N. Gumilyov Eurasian National University, Satpaev str., 5, 010008 Astana, Kazakhstan

³The Ural Federal University named after the first President of Russia B. N. Yeltsin, Mira str. 19, 620002 Yekaterinburg, Russia

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Abstract

In the paper, the catalytic activity of composites based on gold nanotubes and ion track membranes was studied using bench reaction of the *p*-nitrophenol (4-NP) reduction in the temperature range of 25-40 °C. The efficiency of the prepared catalysts was estimated on the rate constant of the reaction and by conversion degree of 4-NP to *p*-aminophenol (4-AP). The comprehensive evaluation of the structure was performed by X-ray diffraction and scanning electron microscopy. A decreasing of the composites activity was observed when the reaction were carried out at the temperature over 35 °C, due to an increased average crystallite size from 7.31±1.07 to 10.35±3.7 nm (after 1st run). In temperature range of 25-35 °C the efficiency of the composite catalyst was unchanged in 3 runs and decreases by 24-32 % after the 5th run. At the high temperature of 40 °C after the 5th run the composite become completely catalytically inert. Copyright © 2018 BCREC Group. All rights reserved

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1. Introduction

Discovery and further first manufacturing of ion track membranes (ITMs) using accelerated heavy ions in the second half of the last century starts a new stage in the development of classical membrane science. Among many types of the polymeric membranes, ITMs is one of the most promising due well-defined geometry of pores – cylindrical, conical or bottle-shaped et al [1], precise pore diameters (10 nm – 5 μ) and narrow pore size distributions [2]. Special at-

tention is paid to the development of the ion track membranes with defined structures [3,4], physicochemical and transport properties [5,6] as well as to its application in different areas of nanoscience. Currently, such composites based on ITMs and metallic nanostructures has an emerging interest in development of sensors [7-9] and ion-selective membranes [10,11], new magnetic materials and devices [12,13], in medicine [14,15] and catalysis [16,17].

Also ITMs with embedded metal nanoparticles/NTs possesses a good catalytic ability in reactions being easily passed over the surface as well as through membrane's channels. The main advantages of ITMs-based composites as highly efficient heterogeneous catalysts are: (a) a wide

* Corresponding Author.
E-mail: mashentseva.a@gmail.com (A.A. Mashentseva)
Telp: +7-707-322-43-99, Fax: +7-7172-34-20-78

range of desired metals/alloys could be easily deposited within the channels of membrane; (b) membrane geometry allow to uniform distribute the catalytically active material over the whole pores surface; (c) possibility to carry out reactions without separation of nanosized catalysts from reaction media after reaction is complete; and (d) polymer template could be easily removed by dissolving in appropriate solvents and the formed nanostructures without morphological changing could be using separately.

Recent literature survey has shown that the catalytic activity of composite membranes could be evaluated with the most well-known bench reaction for evaluation of nanosized catalyst such as 4-NP reduction in presence of sodium borohydride [18,19]. Composite membranes based on ITMs and silver [16,20], gold [21], palladium [22], mixed Ag/Au [23], Au/Pt [24], and Ni-Co [25] NTs possesses a good catalytic ability in 4-NP reduction reaction.

Despite the works conducted to explore the potential of ITMs with embedded metallic NSs for the reduction of 4-NP, a comprehensive study of their structure-catalytic activity relationships has not been conducted so far. Therefore, it was our interest to assess the catalytic activity and reusability of composites based on (polyethylene terephthalate) PET ITMs and gold NTS at the different temperatures, as well as estimate changes in structure by XRD and SEM techniques. The present study underlines the great ability of flexible catalyst-coated membranes to accelerate reaction of the 4-NP reduction.

2. Materials and Methods

2.1 Template Preparation and NTs Synthesis

PET ITMs with nominal thickness 12.0 μm were irradiated at the DC-60 heavy ion accelerator in Astana, Kazakhstan with krypton ions (energy: 1.75 MeV/nucleon, fluence: of 1×10^9 ions/cm²). The irradiated film was etched out for 75 sec in 2.2 M NaOH solution at 85 ± 1 °C. The pore size did not exceed 100 ± 5 nm.

Prior to electroless gold deposition, the PET ITMs were exposed to activation and sensitization procedures [26]. Generally, these stages use surface-bound Sn(II) to reduce Ag(I), leading to the formation of catalytically active silver NPs on the polymer template. For the polymer's surface sensitization all samples were immersed into a solution of SnCl₂ (25 g/L) and hydrochloric acid (60 g/L) for 15 min to and thoroughly rinsed for 15 min under flowing water.

At the next activation stage, the sensitized membrane was immersed for 5 min into Ag-based solution (10 % AgNO₃, 25 % NH₃, and 3 % NaOH) to provide formation of the thin layer of silver nanoparticles [17]. Gold deposition from (Na₃[Au(SO₃)₂]) plating solution was performed for 1 h at pH = 12.0 and temperature 4 °C according to the technique described by Korolkov *et al.* [27]. To dissolve the PET template for gold NTs characterization, the solution of 1,1,1,3,3,3-hexafluoro-2-propanol and chloroform CHCl₃ (1:9 by volume) was used.

2.2 Characterization

For Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) a JEOL-7500F instrument was used. For SEM observation, template-free NTs were collected on the carbon tape sputter-coated with gold. X-ray diffraction (XRD) measurements of the "as-prepared" composite membrane samples were obtained on a D8 Advance (Bruker, Germany). X-ray was generated at 40 mA and 40 kV and the scanning position ranged from 15-90° 2(θ). The crystal grain sizes were calculated using Scherrer equation.

2.3 Catalysis

The catalytic activity of Au-NTs/PET-ITMs composite membranes was determined in the temperature range of 25-40 °C. Testing sample (a square with side 5 cm) was immersed into the stirred reaction mixture of 25 mL of 3.91×10^{-6} M 4-NP and the 3.91×10^{-3} M NaBH₄ aqueous solution. The reaction rate was monitored every 5 minutes using UV-Vis spectrophotometer in the wavelength range 200-600 nm. The residual concentration of 4-NP was determined by using previously prepared calibration curve with formula $y = 0.009x - 0.0001$; $R^2 = 0.9975$. All experiments were repeated five times to prove the recyclability of composite.

3. Results and Discussion

Polymeric ITMs are a flexible and universal template material for the synthesis of highly ordered arrays of metallic nanostructures (in the case of matrix removal) as well as nanocomposites (without separation of NSs from the polymer matrix). SEM images of the synthesized Au-NTs/PET-ITMs composite shown in Figure 1. The deposited NTs were grown through the whole PET template and therefore have a length of 12 μm . The outer nanotube diameter is approximately corresponds to the pore diameter of the template, the inner diam-

eter and wall thickness were determined to be about 60 ± 4.2 and 15.2 ± 5 nm.

A structural and chemical investigation of the prepared composites was carried out with XRD and EDS techniques. According to XRD measurements (see Figure 2a), XRD pattern of Au-NTs/PET-ITMs composite has a main characteristic peaks at 38.14° , 44.42° , 64.25° , and 77.74° related to (111), (200), (220), and (311) planes respectively (JCPDS file N. 04-0784). The predominant peak at $2(\theta) = 38.14^\circ$ is indicative of the predominant orientation (111). Broad peaks in the region 15° to 26° and 53° to 57° are related to the amorphous structure of PET ITMs. The average grain size of the gold NPs on the surface of studied composite was calculated using the Scherrer's formula and presented in the Table 1. EDS (Figure 2a) also confirms that Au is the main component of the prepared composite. Minor fraction of copper (4.2 %) as a material of sample holder was also detected.

Starting from Pradhan [28] reduction of 4-NP by sodium borohydride reaction has been used as a benchmark reaction for the evalua-

tion of catalytic ability of nanosized catalysts [22]. This reaction could be easily monitored by UV-vis spectroscopy: 4-NP shows a characteristic absorption peak at 400 nm in water solution from another hand the product, *p*-aminophenol

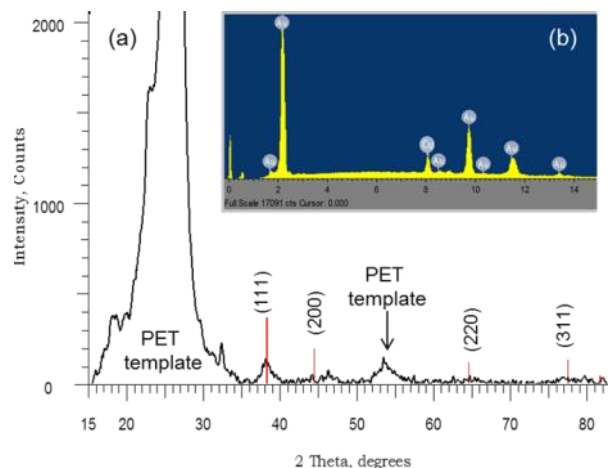


Figure 2. XRD pattern of gold NTs inside the PET template (a) and EDS spectrum of released gold NTs (b)

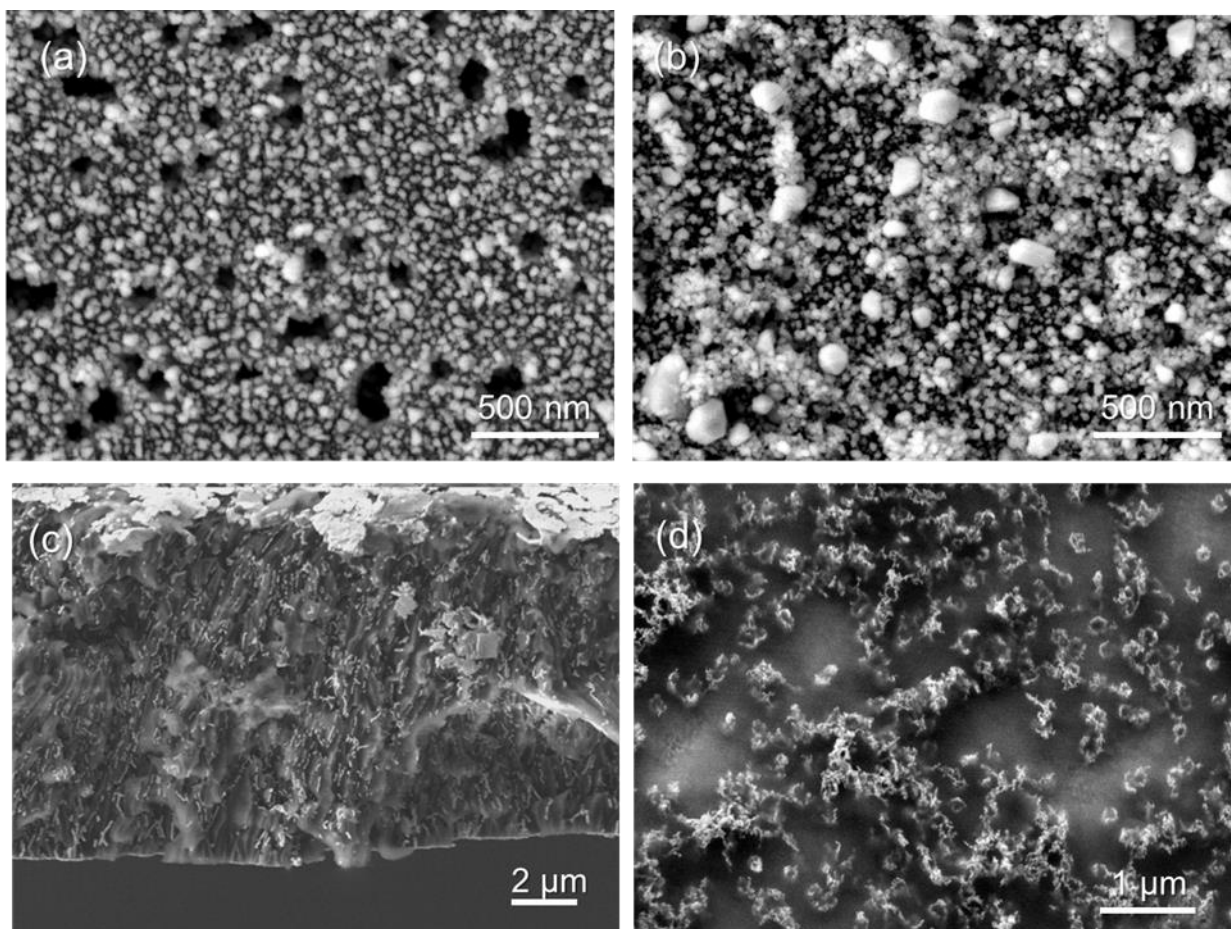


Figure 1. SEM images of Au-NTs/PET-ITMs composite: (a) front side (b) back side, (c) cross-sectional view, and (d) Au NTs after template dissolving

(4-AP), exhibits a weak absorption peak at around 299 nm (Figure 3a). The studied reaction has the pseudo-first order in the presence of excess of NaBH₄, that allows to study the kinetics of the reaction to change the amount of the starting reagent 4-NP (Figure 3b). The slope of a plot of the natural log of the absorbance at 400 nm yields (A_0/A_t) (Figure 3a) allows to calculate the apparent rate constant (k , min⁻¹). It's should be noted, that without the catalyst the reduction of 4-NP does not proceed, even when increasing the duration of the reaction to 120 hours. The values of k as well as data on conversion degree of the 4-NP are shown in Table 2.

The highest value of constant rate and 4-NP conversion degree was observed while testing at the 35 °C. The decreasing catalytic activity after this point could be attributed to the changes of the Au NTs structure in particular it may be caused by increasing of the gold nanoparticles size on the surface/channels of the composite membrane [23]. Increasing of crystallites size was confirmed by XRD analysis of all samples after the 1st run (Table 2). Thus, the average dimension of the Au nanoparticles on the composites surface was increased from 6.99 up to 10.35 nm.

The effect of the high temperature related to the aggregation of gold nanoparticles on the surface of composite membrane was also observed from SEM images are presented in Figure 4. From another hand, previously was reported that NaBH₄ could react to produce hydrogen and boranes and finally to decrease the 4-NP reduction degree [29].

One of the most critical problems for development of the non-supported nanosized catalysts is the need for their separation from reaction media and/or regeneration after every run so a small part of NPs could be removed during these manipulations. Composite and supported catalysts compared to their colloidal counterparts are being used more and more to meet the practical catalytic performance requirements in the chemical industry, such as: high activity and selectivity, as well as reusability and good stability [30]. The reusability of studied composites was examined for 5 times and relation between the number of cycles of the reaction and 4-NP conversion degree is illustrated in Figure 5 (data are shown in this graph are presented with allowance for the standard deviation for three measurements).

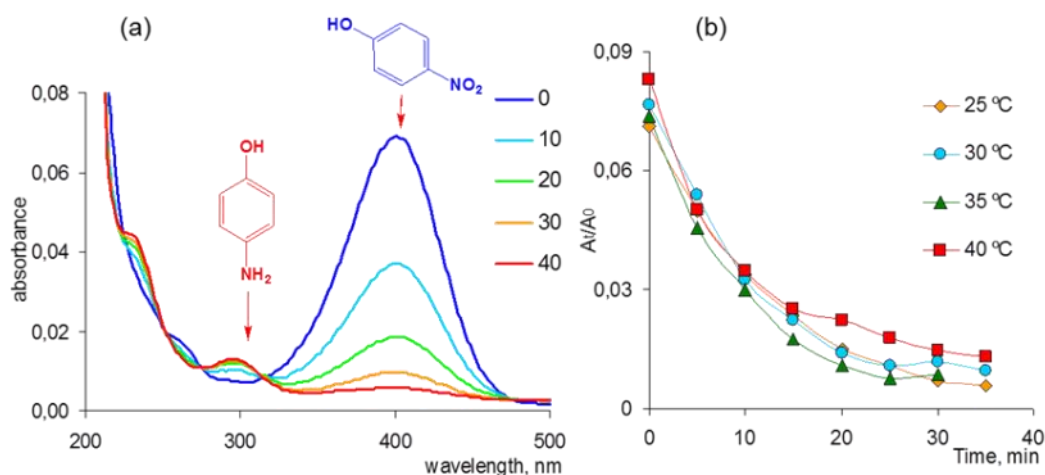


Figure 3. Typical UV-vis spectra of the reduction of 4-NP by sodium borohydride with Au-NTs/PET-ITMs composite membrane (a) and the decreasing of 4-NP concentration at different temperatures (b)

Table 1. XRD data of the pristine Au-NTs/PET-ITMs composite

2(θ), degrees	hkl	FWHM	d, nm	Average size, d, nm	Cell parameter a, Å
38.14	111	1.071	8.20	7.31±1.07	4.080±0.001
44.42	200	1.545	5.80		
64.25	220	1.335	7.34		
77.74	311	1.349	7.90		

In temperature range of 25-35 °C the efficiency of the composite catalyst was unchanged in 3 runs and decreases by 24-32 % after the 5th run. At the high temperature of 40 °C after the 5th run the composite convert only 8 % of 4-NP and become completely catalytically inert.

4. Conclusion

In this study, the influence of operating temperature on structure and catalytic ability

of membrane composites based on ion track membranes and gold nanotubes was demonstrated. The effect of temperature on the catalytic activity was investigated using benchmark reaction of the 4-nitrophenol to 4-aminophenol reduction in the presence of sodium borohydride in temperature range of 25-35 °C. The apparent constant rate of studied reaction k_{app} initially raised with the increase of temperature below 35 °C, which followed the typical Arrhenius-type dependence on tempera-

Table 2. Structural and kinetic parameters of Au NTs/PET-ITMs composite after 1st run at the different temperatures

t, °C	2(θ), degrees	hkl	FWHM	Average size, d, nm	Cell parameter a, Å	$k \times 10^{-2}$, min ⁻¹	Conversion 4-NP, %
25	38.22	111	1.045	6.99±1.6	4.0786	10.00	77.88
	44.556	200	1.914				
	64.54	220	1.278				
	77.49	311	1.481				
30	38.08	111	1.193	7.46±1.8	4.0754	8.97	76.7
	44.32	200	1.816				
	64.89	220	1.097				
	77.54	311	1.237				
35	38.18	111	0.883	9.44±3.4	4.0829	15.32	84.2
	44.34	200	1.587				
	64.54	220	1.177				
	77.42	311	0.769				
40	38.24	111	1.001	10.35±3.7	4.0798	6.00	72.57
	44.32	200	1.503				
	64.67	220	0.687				
	77.44	311	0.859				

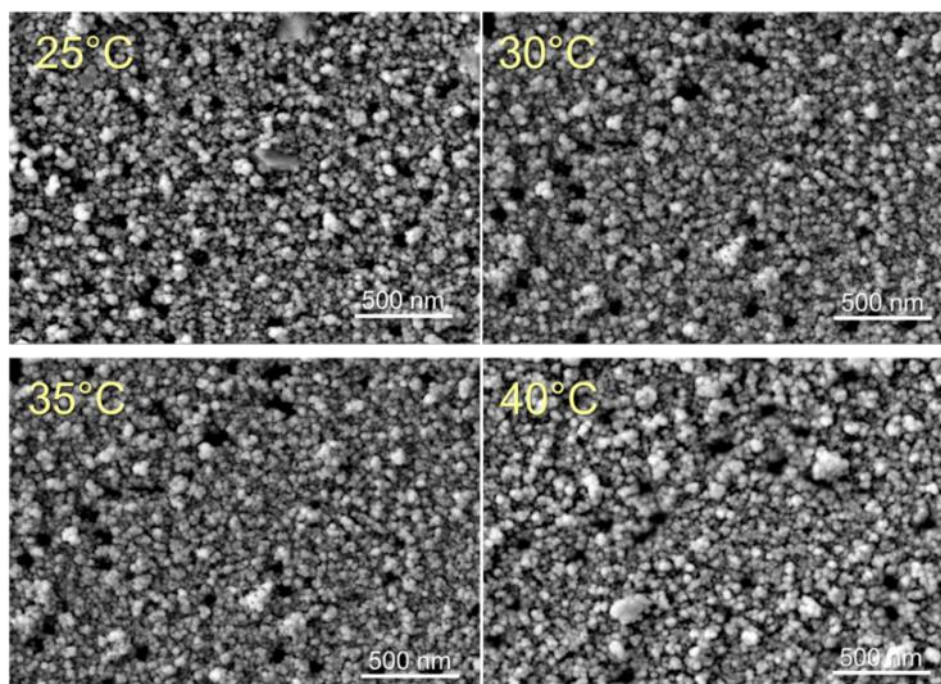


Figure 4. SEM images of Au-NTs/PET-ITMs catalysts after 1st run at the different temperature

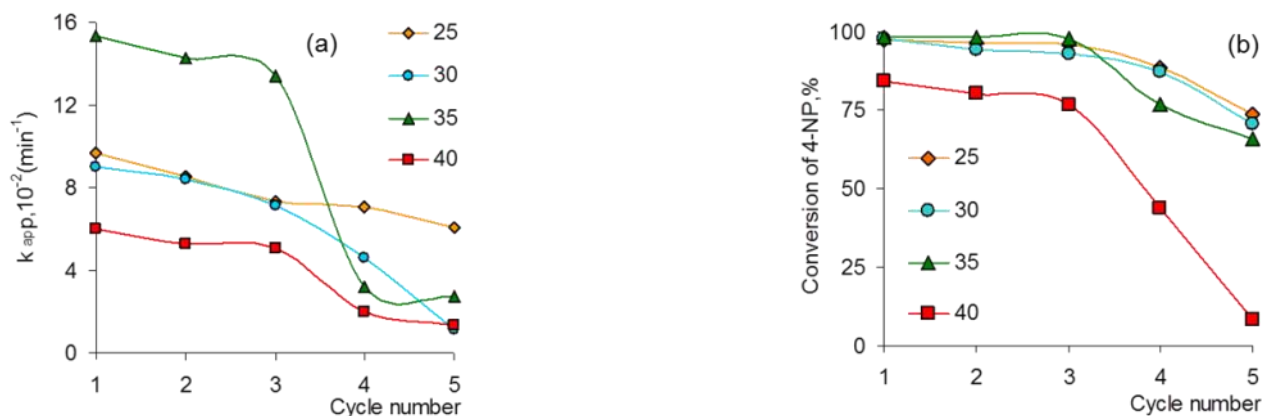


Figure 5. Changing of k_{app} (a) and conversion of 4-NP for five reaction runs in presence of AuNTs/PET-ITMs composite in the temperature range of 25-40 °C

ture. The catalytic activities exhibited dramatically inverse relationship between k_{app} and T at the range from 35 to 40 °C. The possible reason was that the active sites of gold were removed from surface of composite during intensive stirring of the reaction media. The final effect on the morphology, size and aggregation of the gold nanoparticles was confirmed by XRD and SEM. The efficiency of the composite catalyst was unchanged in 3 runs and decreases by 24-32 % after the 5th run (in temperature range of 25-35 °C). At the high temperature of 40 °C after the 5th run the composite convert only 8 % of 4-NP and become completely catalytically inert.

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