Investigation of biological and photocatalytic activity of nanopowders metal oxides with nanosized silver coating

S Yu Sokovnin\textsuperscript{1,2}, V G Il'ves\textsuperscript{1}, O A Malova\textsuperscript{1,2}, M A Kiseleva\textsuperscript{2}, M V Ulitko\textsuperscript{2} and T R Sultanova\textsuperscript{2}

\textsuperscript{1} Institute of Electrophysics UB RAS, Yekaterinburg, Russia
\textsuperscript{2} Ural Federal University, Yekaterinburg, Russia

Email: sokovnin@iep.uran.ru

Abstract. Was carried out the assessment of photocatalytic, cytotoxic properties on cells and antibacterial properties against E. coli and Staphylococcus of oxides nanopowders with nanoscale silver coating. Is shown the promising use of such composites as a photocatalytic agent, as well as in medicine.

1. Introduction
Nanopowders (NP) of silver-coated oxide materials are a promising compound for use in the medico-pharmaceutical sphere due to antimicrobial, antitumor and other properties of the shell and bioinert nucleus.

The purpose of this work is to study the photocatalytic and biological activity of composite nanopowders (NP) Al\textsubscript{2}O\textsubscript{3}, nanosized silver coated SiO\textsubscript{2} produced by radiation-chemical technology (RCT) \cite{1}, and NP Bi\textsubscript{2}O\textsubscript{3} (Ag-Bi\textsubscript{2}O\textsubscript{3}) produced by pulsed electron beam evaporation (PEBE) \cite{2}, to study the prospects for their possible use, including in nanomedicine.

2. Experimental
Depending on the settling time (96 and 15 hours), when producing composites by the RCT, the samples are indicated: Al\textsubscript{2}O\textsubscript{3}Ag\textsubscript{96}, SiO\textsubscript{2}Ag\textsubscript{96} and Al\textsubscript{2}O\textsubscript{3}Ag\textsubscript{15}, SiO\textsubscript{2}Ag\textsubscript{15}, respectively. The nanoparticles sizes of the composites and the proportion of silver coating were: 80 nm, 16-40\% and 50 nm, 2-3\%, respectively.

The mesoporous amorphous crystal HP Bi\textsubscript{2}O\textsubscript{3} containing silver was produced by PEBE in vacuum \cite{2}. The target for evaporation was compressed on a manual press (tablet 40*15 mm) from a mechanical mixture of micron powder Bi\textsubscript{2}O\textsubscript{3} analytic grade (GOST 10216-80) with additives (1 and 5 wt\%) of silver nitrate. The target was pre-annealed on air at the temperature 600°C.

The distance between the target and the glass substrates for collecting NP was 10-15 cm. Evaporation was carried out in the mode: accelerating voltage - 38 kV, beam current - 0.3 A, pulse duration -100 \textmu s, pulse repetition rate - 50 pps, evaporation time - 45 minutes, evaporation chamber pressure - \textasciitilde 4 Pa. The initial NP (sample S0) was then annealed in alund crucibles at 200, 300, 500 and 750°C, further referred to as samples S200, S300, S500 and S750, respectively. The isothermal holding time is 10 minutes, cooling was carried out together with the furnace to 100-150°C.

The textural properties of NP were studied by BET on Micromeritics TriStar 3000 V6.03 A. The pore sizes of NP were 25.1 - 32.5 nm, volume 0.069 - 1.121 cm\textsuperscript{3}/g, specific surface area (SSA) of the
target 1.4 m²/g, SSA of samples 10 - 23 m²/g. A color change was established when heating NP bismuth oxide in the sequence: brown → yellow → red (cherry) → yellow. The occurrence of polymorphic transformations inside the NP and the red color of the powder indicated the possible formation of Bi₂O₃ oxide, which has a bright dark red color.

3. Results and discussion

The method for evaluating the photocatalytic properties of composite powders consisted of the following: the methyl violet dye (MV) was dissolved in distilled water (10 μg/ml concentration). An aqueous 300 μL NP test suspension (for 100 μg/ml NP concentration) consisting of 10 mg NP and 5 mg distilled water and 500 μL (for 300 μg/ml NP concentration) consisting of 20 mg NP and 5 mg distilled water were then added to the solution. The suspension was then irradiated on a UV gas discharge lamp of DRS 250-3 for 40 minutes. The results of the experiments are shown in table 1. The dependence of the discoloration rate of the MV solution on the time of exposure to UV radiation can be described by the linear equation y = kx + b, where the coefficient k is the photodegradation rate (discoloration). The higher the coefficient k, the faster the solution is discolored.

| Sample | k (100 μg/ml) | k (300 μg/ml) | Sample | k (100 μg/ml) | k (300 μg/ml) |
|--------|---------------|---------------|--------|---------------|---------------|
| Test   | -0.02846 (1)  | -0.00963 (1,0) | Test   | 0.02606 (1,0) | 0.03113 (1)   |
| Al₂O₃  | -0.01866 (0,66) | -0.02002 (2,08) | SiO₂   | 0.02257 (0,87) | 0.02533 (0,81) |
| Ag     | -0.01838 (0,65) | -0.02191 (2,28) | Ag     | 0.02066 (0,79) | 0.02608 (0,84) |
| Al₂O₃Ag₉₆ | -0.02052 (0,72) | -0.02334 (2,42) | SiO₂Ag₉₆ | 0.02568 (0,99) | 0.02731 (0,88) |

* parenthetically are the relative values k

It can be seen from the data of table 1 that at the concentration 100 μg/ml NP act as photoprotectors, with the best photoprotective properties observed for Al₂O₃Ag₉₆ and SiO₂Ag₉₆ - i.e. powders with the highest silver area. At the concentration 300 μg/ml, NP showed noticeable photocatalytic properties, with Al₂O₃Ag₉₆ being the most effective. Powders SiO₂, Ag, and SiO₂Ag₉₆ retained photoprotective properties with increasing concentration.

The photodegradation rate of bismuth oxide samples is shown in table 2. It was found that the S300 sample at the concentration 300 μg/ml had better performance, including with silver. High activity is probably caused by annealing of the sample, which reduced the defects in the structure of the NP. It is worth noting that in samples S300 and S750 there is a noticeable discoloration of the solution.

The cytotoxicity of silver-coated oxide nanomaterials was tested in human and animal cell cultures: on Vero green monkey cell culture and human tumor culture HeLa. Cytotoxicity was assessed by cell viability using an MTT test. Studies were conducted at three concentrations (C): 1.5 and 10 μg/ml. The results are shown in tables 3 and 4.

| Sample | Bi₂O₃ | 100 μg/ml | 300 μg/ml | Sample | Bi₂O₃+ Ag, mass. 5 % | 100 μg/ml | 300 μg/ml |
|--------|-------|-----------|-----------|--------|----------------------|-----------|-----------|
| Test   | -0.0249 (1) | -0.0152 (1) | Test     | -0.0148 (1) | -0.0146 (1)         |
| S0     | -0.0295 (1,18) | -0.0264 (1,74) | S0       | -0.0246 (1,66) | -0.031 (2,12)       |
| S200   | -0.0186 (0,74) | -0.0198 (1,30) | S200     | -0.0178 (1,20) | 0.0156 (0,66)       |
| S300   | -0.0208 (0,84) | -0.0265 (1,75) | S300     | -0.0156 (1,18) | -0.031 (2,12)       |
| S500   | -0.0184 (0,74) | -0.0216 (1,42) | S400     | -0.0175 (1,18) | 0.0168 (1,15)       |
| S750   | -0.0198 (0,80) | -0.0159 (1,04) | S500     | -0.0149 (1,01) | 0.0126 (0,86)       |

* parenthetically are the relative values k
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| Table 3. Effect of NP Bi₂O₃ on relative cell HeLa culture viability. |
|---------------------------------------------------------------|
| **Sample** | **Test** | **S200** | **S300** | **S500** |
| C, μg/ml | 1 | 5 | 10 | 1 | 5 | 10 | 1 | 5 | 10 |
| 100 | 97,3± | 79,4± | 74,5± | 99,4± | 83,2± | 67,2± | 97,8± | 73,7± | 72,1± |
| 3,9 | 8,1 | 4,5 | 4,5 | 5,9 | 7,3 | ±5,6 | ±4,4 | ±5,9± |
| Bi₂O₃+ Ag, mass. 5 % | |
| 100 | 95,7± | 76,8± | 64,9± | 92,1± | 70,2± | 50,0± | 92,0± | 71,6± | 48,1± |
| ±2,9 | ±5,1 | ±1,6 | ±6,0 | ±6,0 | ±2,0 | ±7,5 | ±4,1 | ±1,8± |

| Table 4. Effect of NP Bi₂O₃ on relative cell Vero culture viability. |
|---------------------------------------------------------------|
| **Sample** | **Test** | **S200** | **S300** | **S500** |
| C, μg/ml | 1 | 5 | 10 | 1 | 5 | 10 | 1 | 5 | 10 |
| 100 | 87,7± | 53,8± | 39,5± | 84,1± | 49,8± | 36,6± | 78,1± | 38,4± | 33,7± |
| ±4,5 | ±2,6 | ±2,3 | ±2,4 | ±3,3 | ±1,0 | ±5,4 | 3,2 | ±2,6± |
| Bi₂O₃+ Ag, mass. 5 % | |
| 100 | 74,8± | 46,7± | 34,6± | 47,7± | 39,4± | 40,4± | 54,9± | 33,8± | 35,9± |
| ±6,0 | ±2,0 | ±2,8 | ±2,9 | ±1,4 | ±0,9 | ±4,2 | ±2,5 | ±2,5± |

It was revealed that all samples of NP Bi₂O₃ have cytotoxic effect on cages of tumoral and not tumoral origin. At the same time, an increase in the annealing temperature and the presence of silver enhance the cytotoxic effect of NP, both individually and jointly. At concentrations of 5 and 10 μg/ml, tumor cell viability is reduced by 25-40% compared to control. In the case of non-neoplastic cells, a 30-65% reduction in viability was observed at all concentrations (1, 5, 10 μg/ml) compared to the control.

The antibacterial properties of silver-coated Al₂O₃, SiO₂, were tested by the volume displacement method to E. coli and staphylococcus strains, which are indicators of environmental contamination. Sowing of bacterial strains was carried out on meat-and-paste agar. Before the microorganisms were sown, samples of the analyzed NP: Al₂O₃, Ag, SiO₂, composites Al₂O₃Ag96 and SiO₂Ag96 were placed on the surface of the nutrient medium. The microorganisms were then thermostatted and the growth of microorganism colonies around the nanopowder samples was evaluated. NP Ag and Al₂O₃Ag96 showed poor activity against E. coli and staphylococcus, continued research is required [1].

4. Conclusions
Thus, the obtained data show that the investigated NPs are promising for use in nanomedicine and photocatalysis.

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References
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