Design and fabrication of photoactive ZnO-MgO-Ag nanocomposites for medical and environmental applications

N V Nikonorov¹,⁶, S K Evstropiev¹,²,³, A V Shelemanov¹, J F Podruhin¹, V M Kiselev² and A V Karavaeva⁵

¹ ITMO University, Saint-Petersburg, Russia
² JVC RPA “Vavilov State Institute”, Saint-Petersburg, Russia
³ Saint-Petersburg State Technological Institute (Technical University), Saint-Petersburg, Russia
⁴ Saint-Petersburg State Polytechnical University, Saint-Petersburg, Russia
⁵ Saint-Petersburg State Chemical-Pharmaceutical University, Saint-Petersburg, Russia
⁶Corresponding author e-mail address: nikonorov@oi.ifmo.ru

Abstract. Photoactive and bactericidal ZnO-MgO-Ag nanocomposites have been synthesized by liquid polymer-salt method. Polyvinylpyrrolidone plays a double role during nanocomposites synthesis: as the stabilizing component at initial solutions stages and as a fuel during materials calcination. Prepared materials demonstrate the ability to generate chemically active singlet oxygen under UV irradiation. Developed nanocomposites are promising for different medical and environmental application.

1. Introduction
Reactive oxygen species (ROS) play a key role in the photocatalytic oxidation of organic contaminants and in the environmental cleaning and disinfection. The photogeneration effectiveness depends on as the characteristics of exciting light so as on the electronic structure and the photocatalyst morphology. The main problem is that the intensity of this photogeneration often is too low for practical application at the use of the majority of common macroscopic materials.

The photogeneration process includes the generation of different ROS (singlet oxygen, superoxide radicals, hydroxyl radical formation.

ROS formation occurs on the surface and the nanomaterials, having high specific surface area, demonstrate significantly higher photocatalytic and bactericidal properties compared with macroscopic materials. Thus, the materials morphology optimization for the intensification of ROS photogeneration includes the increase of their specific surface area. This can be achieved by the decrease of the semiconductor particles size and/or by the formation of the particles having special morphology.

Solid solutions of ZnMgO, being wide band gap semiconductors (Eg ~ 3÷5 eV) [1], are transparent in near-UV spectral range and have high thermal stability and mechanical strength. Atomic radii of Mg²⁺ and Zn²⁺ are close to each other [2] that provide the crystal structure of these solutions with small amounts of the distortions and local defects. Mixed ZnO-MgO nanostructures prepared by polymer-salt method have homogeneous structure and high specific surface area due to small crystals
size [1]. This determines their effective contact with the surrounding media and high photoactive and bactericidal properties.

It was found that Ag-doped ZnO-based nanocomposites demonstrate the high ability to chemically active oxygen photogeneration and bactericidal properties [3,4]. Thus, based on the previous results [1,3,4] it is possible to conclude that ZnO-MgO-Ag nanocomposites are promising materials for photocatalytic and environmental practical application. In our work we designed and fabricated photoactive and bactericidal ZnO-MgO-Ag nanocomposites by liquid polymer-salt method with the use of polyvinylpyrrolidone.

2. Materials and Methods

Aqueous solutions of Zn(NO$_3$)$_2$, SnCl$_2$, AgNO$_3$ and high-molecular polyvinylpyrrolidone (PVP) (Sigma Aldrich, $M_w$=1300000) were used for powders synthesis.

The drying of the resultant homogeneous liquid mixtures was performed at 20°C. Thermal treatment of dried samples was carried out at atmospheric pressure at 550°C for 2 hours. Chemical compositions of prepared solutions and powders are given in Table 1.

| Sample | Chemical compositions of initial solutions, wt.% | Chemical composition of powders, wt.% |
|--------|-----------------------------------------------|--------------------------------------|
|        | $\text{H}_2\text{O}$ | PVP | Propanol-2 | $\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ | $\text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ | $\text{AgNO}_3$ | $\text{ZnO}$ | $\text{Sn}_2\text{O}_3$ | $\text{Ag}^a$ |
| 1      | 53.27 | 0   | 42.04      | 4.18       | 0.46       | 0.05       | 90.02 | 9.00 | 0.98 |
| 2      | 52.92 | 0.66 | 41.75      | 4.16       | 0.46       | 0.05       |       |     |     |
| 3      | 52.57 | 1.31 | 41.49      | 4.13       | 0.45       | 0.05       |       |     |     |
| 4      | 51.89 | 2.60 | 40.93      | 4.08       | 0.45       | 0.05       |       |     |     |

$^a$All Ag structural forms are taken into account as metallic Ag.

The diffractometer Rigaku Ultima IV was used for XRD analysis of prepared materials. Special experimental luminescence setup was used for the study of singlet oxygen photo-generation in prepared materials. Two different LEDs (HPR40E set) ($\lambda_{\text{max}}$=370 nm; power density 0.35 W/cm$^2$) and ($\lambda_{\text{max}}$=405 nm; power density 0.90 W/cm$^2$) were used for luminescence excitation.

3. Experimental Results and Discussions

Thermal treatment of PVP-based composites at 550°C provided the full decomposition of metals nitrates and PVP and the formation of ZnO-MgO-Ag ceramic composite powders. Figure 1 demonstrates the results of XRD analysis of these powders. Numerous peaks of attributed to hexagonal ZnO crystals (JCPDS card No. 36–1451) and cubic MgO crystals (periclase) (JCPDS card No. 75–1525) are observed in these patterns. The peaks of ZnO crystals are the most intense and the ratio between the intensities of these peaks is close to the standard data (JCPDS card No. 36–1451). The absence of Ag peaks can be related to a small Ag content in prepared materials.

![Figure 1. XRD patterns of ZnO-MgO-Ag ceramic composite powder 4.](image-url)
Average sizes $d_{ZnO}$ and crystals cells parameters of ZnO crystals in ZnO-MgO-Ag ceramic composites were calculated using XRD data (Figure 2; Table 2). Figure 3 shows that PVP additions in the initial mixtures affect the average size of ZnO crystals in ZnO-MgO-Ag ceramic composites. The addition of even small amounts of PVP into initial metals nitrates solutions leads to the observed strong $d_{ZnO}$ decrease.

![Figure 2. Dependence of the average size of ZnO crystals from the amounts of PVP in initial solutions.](image)

It is worth noticing that the morphology and average particle size of oxides obtained by a combustion process depends on the volume of escaping gases forming during heat treatment. Thus, the significant decrease $d_{ZnO}$ at PVP additions into initial mixtures can be attributed to the formation of big volumes of gas products during the oxidation and decomposition of this polymer.

| Table 2. ZnO crystal cells parameters in ZnO-MgO-Ag nanocomposites. |
|---------------------------------------------------------------|
| **Sample** | **ZnO crystal cells parameters** |
|           | $a, b$, Å | $c$, Å | $V_{ZnO}$, Å$^3$ |
| 1         | 3.2392   | 5.1898 | 47.159  |
| 2         | 3.2520   | 5.1941 | 47.572  |
| 3         | 3.2419   | 5.1698 | 47.056  |
| 4         | 3.2465   | 5.1879 | 47.355  |
| JCPDS 01-070-8072 | 3.2465 | 5.2030 | 47.491  |

Figure 3 demonstrates SEM images of the morphology of ZnO-MgO-Ag powders. The powder 1 obtained from the solution without PVP consists of big porous particles having size ~ 10÷20 μm (Figure 3a). Some big hexagonal ZnO crystals are seen at high magnification (Figure 4b) in the powder structure.

![Figure 3. SEM images of ZnO-MgO-Ag nanocomposites 1 (a) and 4 (b,c).](image)

In opposite, the structure of the powder 4 prepared from the solution containing significant amount of PVP (Table 1) is formed from a numerous uniform small (size about 20÷30 nm) nanoparticles.
The size of these nanoparticles is close to the average crystals size obtained from XRD analysis. This difference is explained by the characters of the thermal evolution of raw mixtures during powders synthesis.

The luminescent band with $\lambda_{\text{max.}} = 1270$ nm which is characteristic for singlet oxygen was observed in photoluminescence spectra of ZnO-MgO-Ag powders (Figure 4).

![Figure 4. Photoluminescence spectra (λex. = 385 nm) of ZnO-SnO2-Ag nanocomposites](image)

The singlet oxygen photogeneration proceeds on the surface of photoactive materials. Thus, the significant decrease of ZnO crystals size (and the corresponding growth of their specific area) at the addition of PVP into initial solutions (Figure 4) can be responsible for the observed strong increase of the intensity of singlet oxygen photogeneration. The difference in the powders morphologies is another important factor that significantly affects the intensity of singlet oxygen photogeneration.

### 4. Conclusion

ZnO-SnO2-Ag nanocomposites able to generate chemically active oxygen species under external lighting have been prepared by polymer-salt method. The powders morphology and crystal structure strongly affect the photoactive properties of prepared materials. The addition of polyvinylpyrrolidone into the initial mixtures decreases the average crystal sizes in prepared powders, changes the morphology of the materials, and enhance significantly their ability to generate chemically active oxygen species. The obtained results are promising for photocatalytic and environmental applications.

### Acknowledgment

The work was funded by Russian Science Foundation (research project No. 20-19-00559).

### References

[1] Evstropiev S K, Soshnikov I P, Kolobkova E V, Evtropev K S, Nikonorov N V, Khrebtoy A I, Dukelskii K V, Kotlyar K P, Oreshkina K V and Nashekin A V 2018 Polymer-salt synthesis and characterization of MgO-ZnO ceramic coatings with the high transparency in UV spectral range Opt. Mater. 82 81-87

[2] Huheey J E, Keiter E A and Keiter R L 1993 Inorganic Chemistry: Principles of Structure and Reactivity (New York: HarperCollins)

[3] Evstropiev S K, Nikonorov N V, Kiselev V M, Saratovskii A S and Kolobkova E V 2019 Transparent photoactive ZnO-MgO-Ag2O films on glasses Opt. Spectrosc. 127 314-21

[4] Evstropiev S K, Nikonorov N V, Saratovskii A S, Dukelskii K V, Vasiliev V N, Karavaeva A V and Soshnikov I P 2020 Photo-stimulated evolution of different structural forms of silver in solutions, composite and oxide coatings J. Photochem. Photobiol. A 403 112858

[5] Bagrov I V, Kiselev V M, Evtropev S K, Saratovskii A S, Demidov V V and Matrosova A S. 2020 Singlet oxygen generation in microcapillary optical elements with photoactive coatings Opt. Spectrosc. 128 214-19