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Synthesis, Structure and Biomedical Application of Nanosize Composites Based on Oxide Semiconductor and Metal (Review)

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Today, nanocomposites based on magnetite (Fe_3O_4), zinc oxide (ZnO), titanium oxide (TiO_2) doped with metal cations are widely used to create new kinds of biocompatible materials, which are characterized by unique complexes of physical-chemical properties. The semiconducting-nanoparticles' coating by metals leads to their stabilization in corrosive biological media and affects their electrical, magnetic, catalytic, and plasmonic properties too. The achievements during recent years in the field of producing composites based on nanosize particles of different nature are demonstrated in a given review article. The basic methods for materials' preparation, properties, and the possible fields of their application are summarized.

Сьогодні нанокомпозити на основі магнетиту (Fe_3O_4), оксиду Цинку (ZnO), оксиду Титану (TiO_2), леґованих катіонами металів, широко використовуються для створення нових видів біосумісних матеріялів, що характеризуються унікальними комплексами фізико-хемічних властивостей. Покриття напівпровідникових наночастинок металами приводить до стабілізації їх у корозійних біологічних середовищах і впливає також на їхні електричні, магнетні, каталітичні та плазмонні властивості. Досягнення останніх років у галузі виробництва композитів на основі нанорозмірних частинок різної природи продемонстровано в даній оглядовій статті. Підсумовано основні методи підготовки матеріялів, властивості та можливі сфери застосування їх.

Key words: Fe_3O_4, ZnO, TiO_2, nanocomposites, nanoparticles, structure, conductivity, bactericidal action.

Ключові слова: Fe_3O_4, ZnO, TiO_2, нанокомпозити, наночастинки, структура, електропровідність, бактерицидність.

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1. INTRODUCTION

Nowadays, it will not be an exaggeration to attribute the spread of viral infections and ensure the biological safety of the population to the global problems of the XXI century. According to statistics, every year, 15 million people die in the world. Viral infections have a division into new (emergent) and secondary (re-emergent). The second type includes avian influenza viruses (A (H5N1)) (1997), A (H9N2) (1999), A (H7N7) (2003), A (H7N3) (2004), A (H7N9) A (H10N8) (2013), including pandemic virus A (H1N1) pdm09 (2009), coronaviruses (SARS viruses, 2002, Middle Eastern respiratory syndrome MERS-CoV, 2012), *etc*. The urgency of the research topic is due to the need to develop the latest effective means of preventing the spread of viral pathogens that can lead to epidemics and pandemics.

Functional nanocomposites based on metal oxides as TiO_2, ZnO, and Fe_3O_4 doped with noble metals and rare-earth elements (REE) can be a perspective material for the new kind of bioactive photocatalysts creation, whereas, the presence of REE in the structure of the zinc and titanium oxides enhances their photocatalytic activity. The inclusion of noble metal cations in the crystal lattice of iron oxides enhances their optical properties [1–2]. In addition, effect of UV irradiation on metal oxide catalysts promotes to appearance their photobactericidal activity [1–10].

This paper presents the composite nanomaterials for the development of novel water purification technologies. The unique surface, optical, and catalytic properties of nanomaterials based on oxide nanoparticles of different nature are present to the wastewater treatment. The aim is to analyse the state-of-the-art of the given rapidly developed research area.

2. METHODS OF PREPARATION AND PROPERTIES OF COMPOSITES WITH TiO_2 NANOPARTICLES

In the past 10 years, TiO_2 nanopowder through photocatalytic activity, chemical resistance and non-toxic can be used as an effective agent for the treatment of organic and inorganic substances, pathogens of various types in the environment [7–10]. The unique properties of TiO_2, especially nanoscale one, used to address important energy and environmental issues have caused the recent emergence of large scientific works on the synthesis and study of its antivirus properties and then search for ways of its practical application The antiviral activity of TiO_2 anatase nanoparticles against human adenovirus 5 serotypes was between 45% and 95% dependence on particles size [8].

The authors [1–7] note that the doping by metal (rare earth) elements allows shifting to the visible region, but the photocatalytic activity may decrease, especially in the UV range. For the electronic interaction, nitrogen is good because of electrons can pass for the dopant of the orbitals 2*p* or 3*p* to the 3*d* orbital Ti, and the width of the forbidden band decreases. The photocatalytic activity decrease of doped TiO_2 powders in the visible region, especially in the polluted environment is an urgent problem to solve [10–17].

TiO_2 powders doped with Ag, Fe enhance the photocatalytic and bactericidal activities [20–23]. For example, Ag concentration from 2.46 to 6.0 wt.% showed increasing of bacteriophage virus inactivation rate by 7 times. Therefore, the duration of the disinfection process reduced from 5 to 0.75 min [20]. Der-Shing Lee and Yu-Won Chen have shown the optimum Ag loading (2 wt.%) for the excellent methylene blue destruction under UV-light irradiation [24].

The bactericidal effect on the bacillus Kochi has been studied using TiO_2–Ag–SiO_2 photocatalyst [23]. The synthesized composite characterized by a higher surface area of 164 $m^2 \cdot g^{-1}$ in comparison with P25. Thus, the ability to inactivate composite photocatalyst occurs over a wide spectral range of UV irradiation with an intensity 2.5 mV cm^{-2}. However, the high absorbance of visible light does not always increase the photocatalytic activity. Sometimes, the cation doping leads to a certain number of defects in TiO_2, which can act as centres for the recombination of charges.

Nevertheless, this can be avoided if after doping the photocatalyst is annealed additionally. For example, the annealing of TiO_2–Co photocatalyst at 100, 400, 600, and 800°C for 180 min resulted in 30, 50, 90, and 60% photodestruction of 2-chlorophenol, respectively [25]. Thus, the annealing temperature for doped anatase (500–600°C) increases the crystallinity and reduces the recombination of electron–hole pairs.

The presence of Ti^{3+} defects for the synthesized sample could be the reason for bandgap decrease in this semiconductor to 2.75 eV and growth of MO (methyl orange) anode oxidation currents under UV irradiation at high scan rates (above 50 mV/s) and potentials below 500 mV (SCE) comparing with standard samples [15]. The photoelectrocatalytic activity of samples is defined by the dispersity and form nanoparticles.

Thus, the photocatalytic degradation is an efficient and economical method that attracted increasing attention [20–29]. This is because it is particularly useful for cleaning biologically toxic or nondegradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in wastewater. The contaminant materials are converted largely into stable inorganic compounds such as water, carbon dioxide, and salts, *i.e.*, they undergo mineralization. Additionally, other features such as morphological architecture, the nature of catalyst, and surface properties affecting photocatalysis will be considered when designing a stable and efficient catalyst material.

3. NANOMAGNETITE DOPED WITH NOBLE METALS

Core & shell type nanocomposites are attractive to practical application in biological and medical studies due to the combination of their useful physical-chemical properties such as optical (plasmonic), (super)paramagnetic, catalytic, accompanied with biocompatibility as well.

3.1. Typical Synthesis Methods to Obtain Core and Shell Type Nanocomposites

Generically, the obtaining of core and shell type nanocomposites based on ferromagnetic cores covered with precious (noble) metal shells includes the synthesis of iron oxides nanoparticles and the following formation of noble metal shell on their surface [30]. Nowadays, core & shell type nanocomposites are usually formed *via* as follow:

1) coprecipitation of ferric and ferrous salts in weak-alkaline water dispersion medium and reduction of noble metal shells on their surface [31];

2) microemulsion method [32, 33];

3) separate sedimentation of the nucleating seeds (magnetite and gold) and formation of corresponding composites using organic substance [34].

Less commonly applied methods are closely connected with the x-ray emission [35], laser ablation [36], sonochemical reaction [37], 'wet' chemistry [38], and photochemical reduction [39].

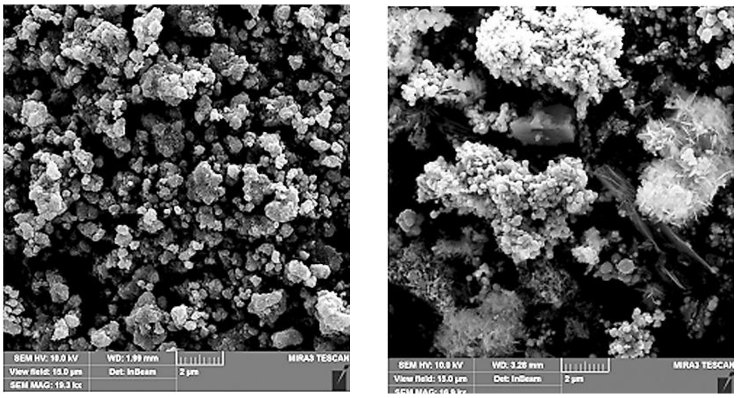
According to published data, the process of the formation of cores and shells is possible in two phases system (microemulsion method), as well as in water [38] or organic medium only [39]. Recently, the combined method including the formation of ferromagnetic core in organic medium and formation of noble metal shell — in water was proposed [40].

The carrying out of the surface separated reductive–oxidative reaction on the steel–solutions of noble metals interface may be referred to alternative synthesis procedure to obtain core and shell type nanoparticles [41]. In the first stage of the process, Fe(II)–Fe(III) layered double hydroxides (LDHs) are formed on the steel surface contacting with distilled water in the open-air system. Taking into account strong reductive properties of Fe(II)–Fe(III) LDHs, their following contact with water medium containing noble metal aqua forms leads to phase transformation of LDH into magnetite particles accompanied with reduction of precious metals on their surface or it leads to the inclusion of Ag, Au, Pt or Pd cations into the crystal lattice of magnetite. The concentration of noble metals in the initial solutions influences degree of a core covering and the thickness of the shell at all. The main advantages of the procedure lie in the simplicity of the method, the absence of necessity to use superficially active substances (SAS), various reducing agents, and high concentrated ferric–ferrous solutions to form core particles as well.

To obtain ferromagnetic cores, it is usually applied co-precipitation in the water medium in the presence of inorganic ferrous and ferric salts and base solution NaOH or NH_4OH under standard conditions [42] or in the nitrogen atmosphere by the addition of a reducing agent, for example, sodium citrate [43]. In addition, the reductant simultaneously plays the role of stabilizing substance [44]. Numerous synthesis methods of obtaining ferromagnetic nanoparticles were described in several reviews [45]. Nanosize iron oxides for biomedical applications are usually obtained *via* polyol synthesis, preparation of microemulsions, co-precipitation, decomposition of organic species, *etc*. Thus, nanocomposites based on iron cores and silver shells were produced under the standard conditions in the solution containing argentum nitrate, ferrous salt, borohydride, and sodium citrate [46]. As the determinative factors of obtaining nanocomposites, the sequence of solutions blending, and time of reagents addition was found.

Hydroxylamine, citrate, or sodium borohydride are most commonly used as reducing agents [47]. To reduce the silver layer onto nanomagnetite surface, tartaric acid was used [48]. However, the application of various SAS and organic components to obtain core and shell type nanocomposites is impossible for structures prepared for biomedicine, so in that case, there are preferable to use various biocompatible substances. For example, Fe_3O_4 and Au particles were synthesized *via* a combination of chemical and biological route [49]. Ethanolic extract of *Eucalyptus camaldulensis* was used to reduce aurum on the magnetite surface from the water solution of $HAuCl_4$.

Therefore, we need to develop effective materials for preventing



a *b*

Fig. 1. SEM images: *a*—TiO_2–Ag (4 wt.%) (×19300); *b*—Fe_3O_4–Ag (×16900).

the bacteria from environmental because of pandemic spreading. The idea is the creation of functional composites based on magnetite and anatase with cations of Ag, Pt, Pd, which exhibit bactericidal and antiviral activities under the UV irradiation for purification water and air.

Functional nanocomposites based on metal oxides as TiO_2, Fe_3O_4 doped with noble metals and rare-earth elements (REE) can be a perspective material for the new kind of bioactive photocatalysts creation, whereas, the presence of REE in the structure of the zinc and titanium oxides enhances their photocatalytic activity [30]. The inclusion of noble metal cations in the crystal lattice of iron oxides enhances their optical properties [31] accompanied by superparamagnetic properties and high catalytic activity for phospholipids.

Our team synthesized bioactive magnetite and anatase doped cations of Ag, Pt, and Pd with a concentration in the interval 0–5 wt.% (Fig. 1). Noble concentrations influence surface structure and magnetic properties of as-prepared and UV-irradiated nanocomposites doped with Ag, Pt, Pd. EDX analysis testifies composition of TiO_2–Ag (Ti—58.6 wt.%, O—36.69 wt.%, Ag—4.12 wt.%) and Fe_3O_4–Ag (Fe—50.84 wt.%, O—44.92 wt.%, Ag—4.3 wt.%).

According to obtained data, the UV irradiation changes the spine quantity in the structure of the nanocomposites and it shifts the characteristically lines to high energy.

3.2. Study of Adsorption and Phagocytosis of Magnetite Particles by U-937 Cells

Our study of the magnetite nanoparticles adsorption and their phagocytosis by U-937 cells was performed using the Lilly cytochemical method. Incubation of U-937 cells with magnetite particles was performed in phosphate-buffered saline for 15–120 min. According to the obtained data (Fig. 2), magnetite with a nanometer particle size is adsorbed on the cell surface and does not show signs of phagocytosis. The obtained data indicate that, during the entire period of observation in the cells of the control group, there were not detected granules, which include Fe^{2+} and/or Fe^{3+}.

Magnetite obtained on the surface of the iron with particles size 1 μm was identified on the cell surface in the form of both aggregates and individual particles. For 15 min of incubation at the point of contact of magnetite with the cell, there was observed bending of the cytoplasm. Phagocytic magnetite particles are also present in some cells. The amount of phagocytosed and adsorbed magnetite in the cells increased during 2 h of observation. The adsorption of natural microsize magnetite by the cell surface is similar to the ad-

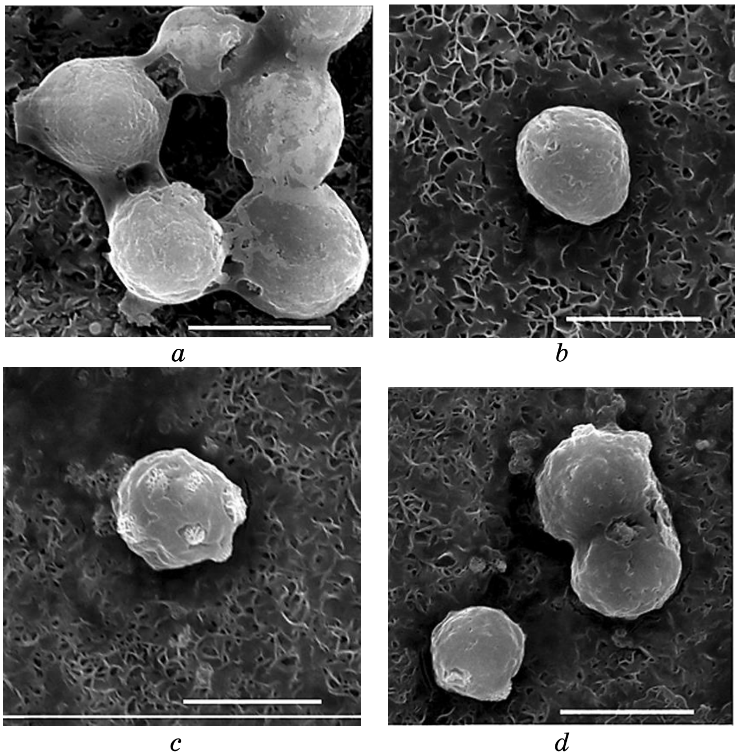


Fig. 2. Cells of the U937 line (human leukemic monocyte lymphoma cell line): *a*, *b*—system cells; in-cells after incubation with nanosize magnetite particles; *c*, *d*—cells after incubation with microsize particles of magnetite. Notice: scale is 10 μm.

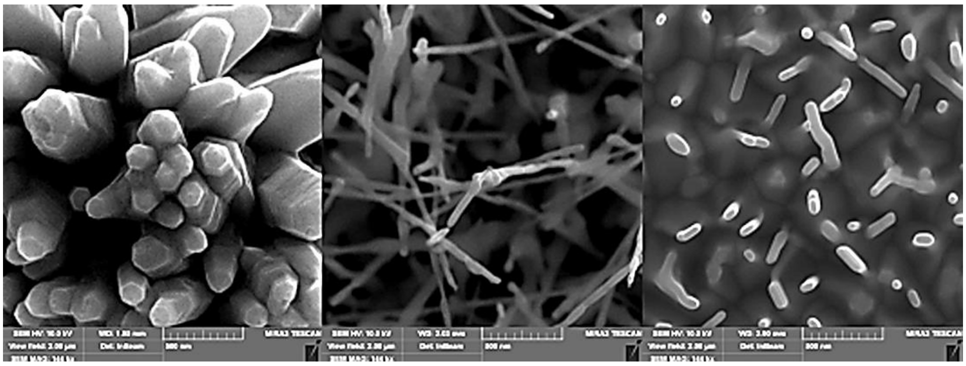
sorption of the synthesized analog, but during 120 min of incubation, the amount of phagocytosed and adsorbed natural magnetite in the cells increased and exceeded the values obtained for artificial magnetite. Moreover, in some cells, phagocytosis was accompanied by cell death and disintegration. Based on the obtained results, it is concluded that the magnetite obtained by the method of rotational corrosion dispersion has less biological activity compared to natural and this makes it suitable for further use in various biological systems.

Thus, the study of the interaction of tumour cells of the promonocytic leukaemia line U-937 with magnetite particles obtained by the method of rotational corrosion dispersion, as well as microsize particles of natural magnetite proved their lack of cytotoxic properties. The revealed dependence of the cytotoxic activity of other iron-oxygen-containing minerals on their nature and particle size is due to a possible criterion for the selection of ferromagnetic material concerning its suitability for medical and biological research. Nanosize magnetite particles form a complex with transferrin, a natural transporter of iron, and accumulate in mitochondrial and cytosolic cell fractions. The tested particles of iron–oxygen-containing minerals are recognized as suitable for the creation of nanosize magnetic carriers.

4. MANUFACTURING AND PROPERTIES OF ZnO NANOSTRUCTURES

Among the metal oxide nanoparticles (NPs), ZnO a wurtzite *n*-type semiconductor and which have potential material for biosensing and gas sensing application because of their unusual properties, like direct bandgap (3.37 eV), high exciton binding energy (60 meV), and resistivity (10^{-4} to 10^{5} $\Omega\cdot$cm), including high surface area, high catalytic efficiency, nontoxicity, chemical stability, and strong adsorption ability. ZnO nanostructures (NS) due to their unique properties have the possibility of using in the ultraviolet (UV) photodiodes, piezoelectric devices, chemical sensors, *etc.* [50]. In the last years, ZnO has been more actively studied as a cost-effective and eco-friendly photocatalytic material for the cleaning of the environment from persistent organic pollutants, bacteria [51, 52]. ZnO films and nanostructures were deposited on Si substrates by MOCVD using single-source solid-state zinc acetylacetonate (Zn(AA)) precursor [53]. Doping by silver was realized in-situ *via* adding 1 and 10 wt.% of Ag acetylacetonate (Ag(AA)) to zinc precursor. The MOCVD method of growth allows us to deposit the different types of ZnO nanostructures morphologies (Fig. 3).

It was shown that Ag doping affects the ZnO microstructure *via*



a *b* *c*

Fig. 3. SEM images of ZnO:Ag nanostructures: nanorods (*a*), nanowires (*b*) and nanoteats (*c*) deposited on Si substrates.

changing the nucleation mode into heterogeneous and thus transforming the polycrystalline films into a matrix of highly *c*-axis textured hexagonally faceted nanorods or nanowires. Ag doping leads to increasing of the work function value from 4.45 to 4.75 eV that is attributed to Ag behaviour as a donor-type impurity. It was observed that near-band photoluminescence of ZnO NS was enhanced with Ag doping because of quenching deep-level emission. Observed considerable amplification of near-band photoluminescence in Ag-doped ZnO NS comparison with undoped ZnO may be caused by surface plasmon resonance, which, as we believe, can be used for the development of the effective photocatalytic devices based on Ag-doped ZnO NS for the disposal of the environment from organic pollutants and bacteria, *etc*.

Besides, the nanosize ZnO particles having a large specific surface and high surface energy, upon settling on the surface of a bacterium, easily destroy the cell membrane and penetrate the microorganism. In this case, the balance of metabolism and energy with the environment is disturbed, and the bacterium death occurs. To increase the bactericidal activity of ZnO-based nanostructures, all types of modifications are used [50–54]. Thus, the creation of structures of ZnO/Au, Ag, Cu leads to an increase in the ROS (super radical oxides) release rate due to the separation of electron-hole pairs at the Schottky barrier and decrease in their recombination, acceleration of the generation of such pairs caused by the influence of surface plasmons and the shift of the absorption edge towards the visible light. In such structures, charge transfer from Au and Ag to ZnO can cause an electrostatic attraction between positively charged metal particles and negatively charged bacteria, increasing bactericidal activity. In addition, noble metals themselves have bactericidal properties of a wide spectrum of action.

The authors of chapter [54] discussed the application of various nanomaterials (such as metal nanoparticles, metal oxides (TiO_2, ZnO, CeO_2, Fe_3O_4), carbon compounds, filtration membranes, *etc.*) in the field of wastewater treatment by photocatalysis. In the last years, most photocatalysts have been specifically devised for application under sunlight, but many researchers focused attention on UV-active systems [54]. Thus, here, we will differentiate between UV- and visible light or sunlight-active nanoscale semiconductors. This chapter [54] also includes a description of the most studied photocatalytic reactions related to water purification, the degradation of emerging pollutants, and disinfection procedures.

Considering the methods of synthesis and study of nanocomposites properties with oxide NPs, especially of TiO_2, has not yet received information on the effectiveness of their use. The reason for all would be to use expensive Ti precursors. Using cheap $TiCl_4$ as the precursor of TiO_2 does not allow us to obtain the composite system with the required properties due to the complexity of the control of the hydrolysis process, the difficulties associated with the removal, and the highly reactive reaction by-products (HCl). However, methods of the TiO_2-surface modifying in the synthesis of composites do not cause difficulties in most cases and could be successfully applied to industrial processes.

Thus, it is a global task to create a composite photogenerator based on TiO_2, ZnO, Fe_3O_4 to control the distribution of $h+$ (generation), and then applying for the effective destruction of toxic organic substances and pathogen microorganisms due to the high concentration of oxide radicals.

5. SUMMARY

Thus, nanosize core & shell type composites containing iron oxide cores (magnetite or maghemite) and noble metal shells (in particular gold or silver) are one of the most perspective materials for biomedical applications due to combinations of magnetic, optical, colloid-chemical properties, as well as because of the possibility to biofunctionalization of the surface of the composite. The variation in the physicochemical characteristics of nanocomposites based on ferrimagnetic cores and a noble metal shells opens for us great possibilities for their usage as a platform for the development of highly effective diagnostic and therapeutic tools with selectivity at the level of individual cells and biomacromolecules. The superparamagnetic properties of Fe_3O_4 and Ag^0 shell composite particles and the photocatalytic properties of TiO_2 nanopowder in combination with the bactericidal and antiviral activity of both, which can be significantly increased under the influence of UV radiation, are the basis for the creation of new protective composite materials. Variation in the material composition of such a composite, the structure of oxide particles and the form of their composition of modifying components will optimize the photoactive composite system, which will show the greatest antiviral activity initiated by the action of UV radiation. The obtained nanocomposite (in the form of powder or film) can be used in the creation of technical means and prevention of the spread of infectious diseases in a confined air environment (transport, public places, and hospitals).

Summarised results show that the photocatalysis of composites TiO_2, ZnO appears to be an interesting approach to water purification, offering the possibility of using sunlight as a sustainable and renewable source of energy. This technology is based on the presence of a semiconductor that can be excited by light with energy higher than its bandgap, inducing the formation of energy-rich electron–hole pairs that can be involved in ORR (oxygen reduction reaction). Recent progress has explored the chemical nature of nanoscale semiconductors to improving their electronic and optical properties, enhancing their photoresponse to visible light. In addition, nanomaterials typically have high reactivity and a high degree of functionalization, large specific surface area, size-dependent properties, *etc*. They can application in water purification.

During doping by Ag, important work function to our TiO_2, Fe_3O_4, and ZnO has, and maybe, the transfer of electron will take place from Ag to conducting band oxide to achieve Fermi level equilibrium following by localized surface plasmon resonance. The features of proposed with us doped oxide nanoparticles (specific nanostructures) due to catching and holding of microorganisms, generation of oxidizing radicals by photocatalysts under UV irradiation, mechanical damaging of microorganisms, and inactivation of microorganisms. We are going step-by-step to discover all components and deliver all evidence of such a concept for the effective antimicrobial guard.

However, the questions that have arisen since the start of the COVID-19 coronavirus pandemic, which spreads mainly with air droplets, suggest that scientists will soon turn their attention to cleaning the water and air from microbiological contaminants. By taking into account the advantages of the photocatalytic properties of ZnO over TiO_2, one can expect the problems that have arisen to be solved in particular thanks to zinc-oxide nanomaterials.

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