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TARGETED REQUIREMENTS FOR BIOMEDICAL NANOMATERIALS BASED ON DISPERSED OXIDES AND TEXTILES MODIFIED WITH METAL NPs

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This article analyses some literature data and the authors' developments in the technology of creating of therapeutic depots in the form of films, dispersions of metal oxides and textiles with immobilized biocompatible silver nanoparticles (NPs) in the structure of SiO_2, TiO_2, cotton, biopolymers (alginate, chitosan, lignin, etc.), that have biocidal action, and future trends in this area. We and other researchers have developed methods for the synthesis of photocatalytically active TiO_2 and SiO_2 films, modified with gold/silver/copper NPs, suitable for medical use. An economical and simple low-temperature methods of manufacturing antimicrobial textiles by photo- or thermal activation and the possibility of their multiple use have been developed. The production of biomedical textiles is recently focused on the widespread use of non-toxic biopolymers, combined with textile. We have obtained compositions based on nanodispersed silica with polysaccharide sodium alginate and silver NPs with pronounced hemostatic and bactericidal properties. Obtaining a hybrid material based on a bactericidal textile combined with a dispersed oxide is promising for additional absorption of toxins and wound cleaning. The creation of such universal multifunctional materials includes their high bactericidal and antiviral multiply use. Hybrid materials based on metal NPs in the structure of carriers of different nature as films and dispersions of biocompatible oxides, biopolymers, textiles have a protection against possible toxic effects of nanoparticles and metal ions, self-cleaning capability, photocatalytic, hemostatic properties, temperature resistance, and other. The development and application of such materials is growing rapidly. So, materials based on Ag/SiO_2 dispersions have high antibacterial and antiviral action (single application). Ag/SiO_2 films can act as durable antibacterial cover.

There is an enhancement in the antibacterial properties of Ag-TiO_2 NPs under visible light irradiation and the photocatalytic effect under UV light (single application in the powder form). Self-cleaning, antimicrobial and UV-protective properties have Ag-TiO_2 NPs in textile. Cotton modified with MeNPs demonstrates high efficiency of destruction of bacteria E. coli, K. pneumoniae, E. aerogenes, P. vulgaris, S. aureus, C. albicans, etc., with saving of biocidal activity after 5 cycles of washing. The dynamics of silver ions release from the surface of NPs in the structure of textile upon their contact with water for 72 hours have been studied. The number of irreversibly bound particles in textile structure is sufficient for subsequent use. Modified fabrics are reusable. Composites based on metal NPs in the structure of silica or titania in the presence of biopolymers are effective hemostatic agents with a bactericidal effect. Sodium alginate has a reducing and stabilizing effect on nanoparticles, and silica prevents agglomeration of metal NPs in the resulting composite.

However, it is quite difficult to satisfy the numerous target requirements for biomedical nanomaterials based on metal NPs in the composition of dispersed oxides as well as textiles and/or biopolymers ("all in one") to obtain a single universal multifunctional material that does not lose its properties during operation. It makes more sense to produce composites for purpose targeted applications, such as bactericidal and antiviral, hydrophobic coatings for laboratory surfaces, package and so on. Researches in this area are in progress.

Keywords: *metal nanoparticles (NPs), metal oxide nanoparticles (MeONPs), biopolymers, colloids, SiO_2 films, TiO_2 nanoparticles, SiO_2 dispersions, textile, bactericidal activity, hemostatic properties*

The creation of new bactericidal and medicinal materials with prolonged action is an urgent task of biochemistry, medicine and pharmacology. The purpose of this work is to analyze literature data and the authors' developments in the technology of creating therapeutic depots in the form of films and/or dispersions of metal oxides and textiles with immobilized biocompatible silver nanoparticles (NPs) in the structure of SiO_2, TiO_2, cotton, biopolymers (alginate, chitosan, lignin *etc*.), that have biocidal action, and future trends in this area. We and other researchers have developed methods for the synthesis of photocatalytically active TiO_2 and SiO_2 films, modified with gold/silver/copper NPs, suitable for medical use [1–5]. An economical and simple low-temperature methods of manufacturing antimicrobial textiles by photo- or thermal activation and the possibility of their multiple use have been developed. The production and use of biomedical textiles is recently focused on the widespread use of non-toxic biopolymers, combined with textile [6]. We have obtained compositions based on nanodispersed silica with polysaccharide sodium alginate and silver NPs with pronounced hemostatic and bactericidal properties [7]. Obtaining a hybrid material based on a bactericidal textile combined with a dispersed oxide is promising for additional absorption of toxins and wound cleaning. Prospects for the creation of such universal multifunctional materials include their high repeated bactericidal effect, protection against possible toxic effects of nanoparticles and metal ions, self-cleaning ability, protection against UV-radiation, photocatalytic, antistatic, hemostatic properties, as well as acids, alkalis, moisture and temperature resistance, and corrosion of metal NPs (see scheme [8], Fig. 1). The development of such materials is growing rapidly.

Furthermore metal oxide NPs (MeONPs) have been identified as novel phytomedicine and have recently peaked a lot of interest due to their potential applications in combating phytopathogens, besides enhancing plant growth and yields [9], Fig. 2.

Targets of antibacterial mechanisms by Ag nanoparticles (NPs) are shown in the Fig. 3 [10].

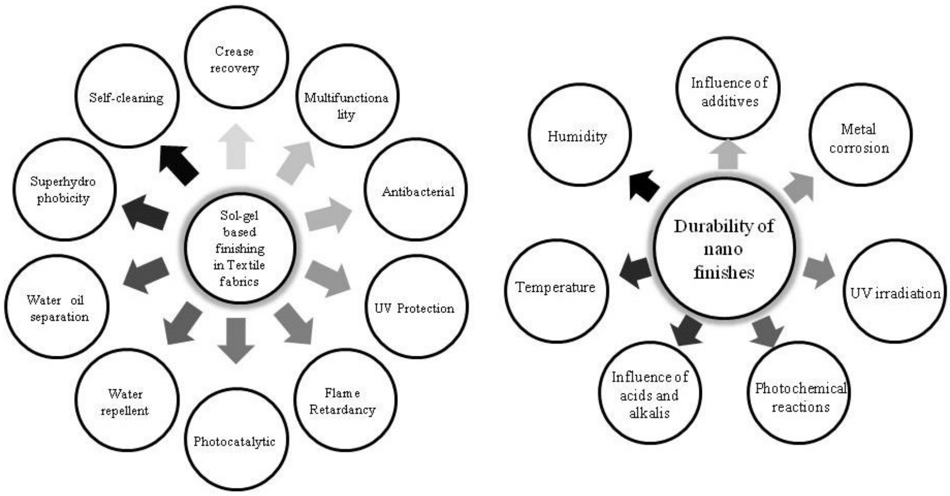

Fig. 1. The main requirements for universal multifunctional bionanomaterials [8]

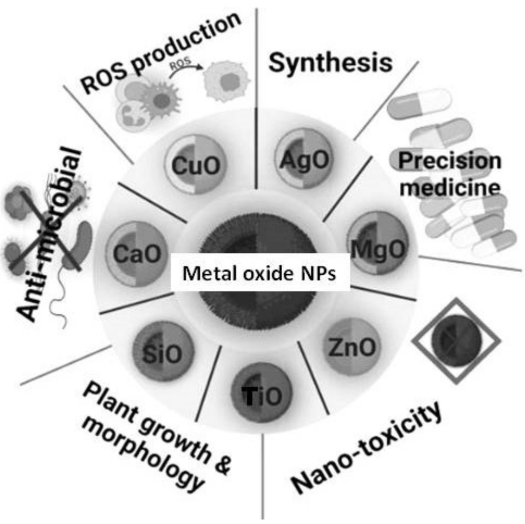

Fig. 2. Potential applications of metal-oxide NPs as bionanomaterials [9]

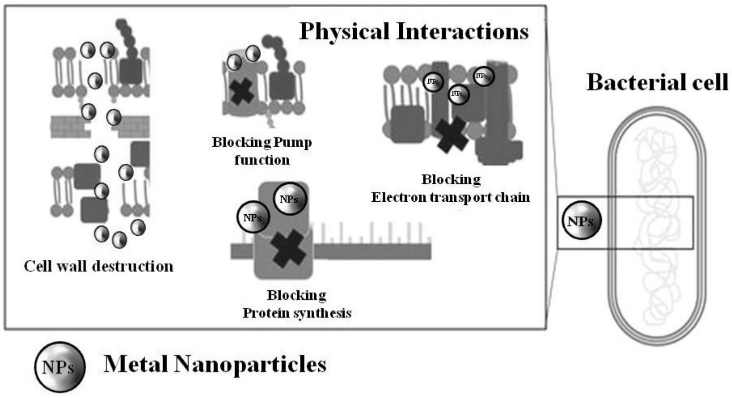

Fig. 3. The stages of the destructive effect of NPs [10]

The destruction of microorganisms is also due to the ROS produced by NPs [11] and release of Ag^+ ions and the induction of antibacterial activity [12].

AgNPs/SiO₂. Metal nanoparticles embedded in dielectric matrixes are promising composite materials for medical application. SEM images of Ag /SiO_2 composites are shown in Fig. 4.

Fig. 4. *a* – SEM image of Ag 2 %/SiO_2 film, *b* – SEM image of dispersed Ag(0.0016 %)/SiO_2 [13]

Essential reduction value for bacteria *E. coli* (5 lg) and fungi *C. albicans* (4 lg) in colloids achieved after 1 hour of exposure of microbial cells with Ag NPs. Embedding of Ag NPs on SiO_2 surface slightly decrease activity of Ag/SiO_2 suspension. The exposure time increases and changes in interaction character of Ag NPs with the microbial cells appear [2]. At the same time Ag/SiO_2-resistance of *E. coli* rised. On the contrary, *S.aureus* was more sensitive than in colloid. But generally antimicrobial activity of Ag NPs/SiO_2 complex remained high. One of the most promising types of such materials is based on a SiO_2-Ag composite immobilized in a polymeric matrix, which has properties that are individually not achievable for each of the components. Here, a plasmonic SiO_2-Ag composite immobilized in a polymeric matrix (ethyl vinyl acetate) was successfully prepared and the as-fabricated samples exhibited high antibacterial activity towards *E. coli* and *S. aureus* as well as towards SARS-CoV-2 [3]. The enhancement is mainly due to the SPR effect of the Ag NPs anchored onto the SiO_2 [14]. The compositions with pronounced hemostatic and bactericidal properties based on nanodispersed silica with sodium alginate (10 % SiO_2) and Ag nanoparticles (NPs) or silver ions (0.02–23 wt. %) have been synthesized [7]. It is shown that the presence of silica in the matrix of sodium alginate promotes the formation of silver NPs of smaller size and prevents their agglomeration. The bactericidal action of hybrid composites against a number of bacteria (*E. coli, K. pneumonia, P. aeruginosa, S. aureus, C. albicans*) was determined, which correlates with the number of released silver ions from the surface of powders upon their contact with water and is optimal at a silver content of 3%. In experiments on rats with parenchymal bleeding high hemostatic activity of obtained compositions has been demonstrated [7].

Application: Ag/SiO_2 dispersion – antibacterial and antiviral action, single application. Ag/SiO_2 films – durable antibacterial cover.

Ag- and Ag/Cu TEXTILE. Synthesis, physicochemical and bactericidal properties of AgNPs/cotton and Ag/CuNPs/cotton fabrics are detailed in a recent review [13]. SEM images of obtained samples are shown in Fig. 5. Cotton samples modified with Ag NPs and Cu NPs have strong antibacterial activity against *Staphylococcus aureus* and *Klebsiella pneumonia* and good antiviral activity in relation to vaccinia virus (VACV), herpes simplex virus type 1 (HSV-1) and influenza [15]. When bacteria or viruses are on the copper surface, Cu ions damage the cell membrane or viral envelope. The destroying of microbes is accelerated by the forming of free radicals due to it having a free electron in its outer orbital shell of electrons that easily takes part in oxidation-reduction reactions [16–18]. Antiviral cotton fabrics impregnated in chitosan, citric acid, and copper are effective against HSV-1 and bovine beta-coronavirus [19]. The difference in antimicrobial ability between Ag and Cu NPs was initially thought to depend on the different amounts of ions released. The activity of Cu was found to be greater than that of Ag, and, at the same NPs concentration, ions released from Cu NPs were found to be at a higher concentration. However, the antimicrobial capability of Ag NPs was found to be greater than that of Cu NPs, indicating that Ag ions are more efficient in antimicrobial activity than Cu ions. Ag NPs also show broader antimicrobial effectiveness to various strains of *E. coli* and *S. aureus*, as well as to fungi which may be due to their stronger interaction with polysaccharides and proteins on cell walls. The existence of an oxide layer on Cu NPs was proposed to be the reason that the antimicrobial capacity of Cu NPs is less than that of Ag NPs [20].

Fig. 5. SEM image of *a* – Ag/cotton and *b* – Ag/Cu cotton fabrics

Authors [15] investigated the effect of two different textile woven structures (polyester (PET) and 100 % cotton (Co) modified by magnetron sputtering with copper (Cu) on bioactive properties against Gram-positive and Gram-negative bacteria and four viruses. PET/Cu and Co/Cu fabrics have strong antibacterial activity against *Staphylococcus aureus* and *Klebsiella pneumonia*. Co/Cu fabric has good antiviral activity in relation to vaccinia virus (VACV), herpes simplex virus type 1 (HSV-1) and influenza A virus H1N1 (IFV), while its antiviral activity against mouse coronavirus (MHV) is weak. PET/Cu fabric showed weak antiviral activity against HSV-1 and MHV. The mechanism of antimicrobial activity of copper is complex. When bacteria or viruses are on the copper surface, Cu ions damage the cell membrane or viral envelope. The destroying of microbes is accelerated by the forming of free radicals. Warnes and co-authors state that copper is more effective in antimicrobial activity than other used metals, due to its having a free electron in its outer orbital shell of electrons that easily takes part in oxidation-reduction reactions [16–18]. Favatela and co-workers tested antiviral cotton fabrics impregnated with different formulations based on chitosan, citric acid, and copper against HSV-1 and bovine, beta-coronavirus (BCoV), and found good antiviral activity against HSV-1 and BCoV [19].

Application: textile modified with MeNPs demonstrate high efficiency of destruction of bacteria *E. coli*, *K. pneumoniae*, *E. aerogenes*, *P. vulgaris*, *S. aureus*, *C. albicans*, etc., with saving of biocidal activity after 5 cycles of washing. The dynamics of silver ions release from the surface of NPs in the structure of textile upon their contact with water for 72 hours and the number of irreversibly bound particles have been studied. Modified fabrics are reusable.

***Ag NPs /TiO_2*.** Me NPs deposited on titania surfaces, embedded within pores or encapsulated in its matrices are expanding applications in medical diagnostics, analytical chemistry, photocatalysis *etc*. The metal NPs, being adsorbed or incorporated into titania matrix, modify the interface and/or alter the pathways with which photogenerated charge carriers undergo recombination or surface reactions. Bare TiO_2 significantly has a weak antibacterial activity while Ag loading to TiO_2 matrix led increase in inhibition area where it diffuses radially outward through the agar, producing zone of inhibition. However, increasing the silver concentration in TiO_2 showed not much effect towards zone of inhibition. Optimum amount of silver was needed to rapidly trap electron. Too much silver may cover the titanium dioxide and prevent light absorption. In addition, too much silver may mean that the silver acts as a recombination site itself and as a result a decrease in photocatalytic efficiency [21]. The significant enhancement in the antibacterial properties of Ag-TiO_2 NPs under visible light irradiation is related to the effect of noble metal Ag by acting as electron traps in TiO_2 band gap [2, 22, 23]. The phase structure, crystallite size and crystallinity of TiO_2 also play an important role in antibacterial activity. Under ultraviolet light, the photocatalytic activity of the TiO_2/Ag NPs could create $\bullet O_2^-$ and OH• free radicals [24–26].

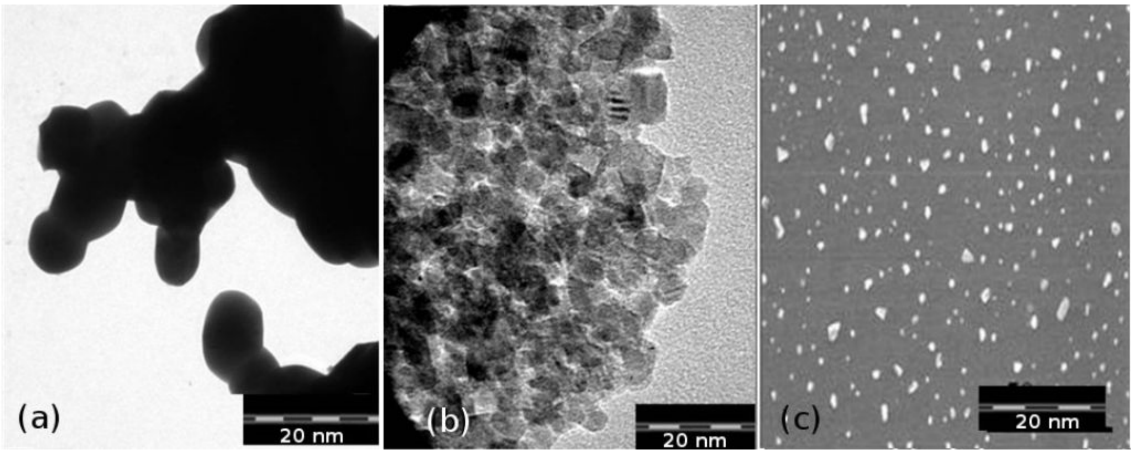

Fig. 6. TEM images of (*a*) TiO_2 and (*b*) 3 % and (*c*) 7 % Ag-doped TiO_2 nanoparticles annealed at 450 °C [27]

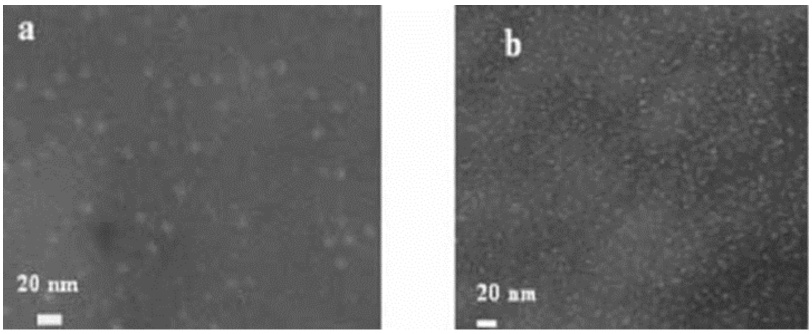

Fig. 7. SEM images of mesoporous films sintered at 500 °C: *a* – SiO_2/Ag 10 % and *b* – TiO_2/Ag 10 % [2]

The silver polymeric nanocomposite (Ag/TiO_2 NPs) embedded in (3-mercaptopropyl) trimethoxysilane (MPTS) and tetraethylortho silicate (TEOS) (TEOS–MPTS–Ag/TiO_2 NPs) has stronger antibacterial activity than Ag/TiO_2 NPs and Ag NPs with a low Ag^+ release [28]. The photocatalysis efficiency of TiO_2 and Ag-doped TiO_2 was tested by the percentage viability against both gram positive *(Staphylococcus aureus)* and gram negative *(Pseudomonas aeruginosa, Escherichia coli)* reduction of bacterial colonies under visible-light irradiation. The pure TiO_2 (crude and annealed) nanoparticles showed poor biocide activity, while doping of silver ions improves the efficiency under visible-light irradiation. The antimicrobial activity of TiO_2 and Ag-doped TiO_2 nanoparticles

(3 % and 7 %) was reduced to zero at 60 mg/30 mL culture [29].

Application: enhancement in the antibacterial properties of Ag/TiO_2 NPs under visible light irradiation. The photocatalytic effect under ultraviolet light. Single application in the powder form. Self-cleaning, antimicrobial and UV-protective properties in textile surface.

Ag NPs/SiO_2/biopolymers. Polysaccharides from natural polymers are widely used as materials for wound dressings due to their low toxicity, good biocompatibility, degradability and reproducibility. Chitosan is a polycationic biopolymer, which has a wide spectrum of biological activity against bacteria, fungi; as well as it has haemostatic properties. Alginate has been used in wound dressing, as it is high absorbent material; therefore it is very appropriate for highly exuding wounds. Alginate in combination with Chitosan are highly absorbent with antimicrobial properties [30–32]. Fig. 8 shows the chemical structure, bioactive groups, monosaccharide units and sites that can be used for biological modification of conventional polysaccharides (chitosan, starch, alginate and hyaluronic acid) [7, 32, 33]. The compositions with pronounced haemostatic and bactericidal properties based on nanodispersed silica with sodium alginate (10 % SiO_2) and silver nanoparticles (NPs) or Ag ions (0.02–23 wt. %) are synthesized. As revealed, the presence of silica in the matrix of sodium alginate promotes the formation of silver NPs of smaller size and prevents their agglomeration. The bactericidal action of hybrid composites against a whole number of bacteria (*E. coli, K. pneumoniae, P. aeruginosa, S. aureus, C. albicans*) is determined; it correlates with the number of released Ag ions from the surface of powders upon their contacting with water [34] and is optimal at the Ag content of 3 %. In experiments on rats with parenchymal bleeding, high hemostatic activity of obtained powder compositions is demonstrated.

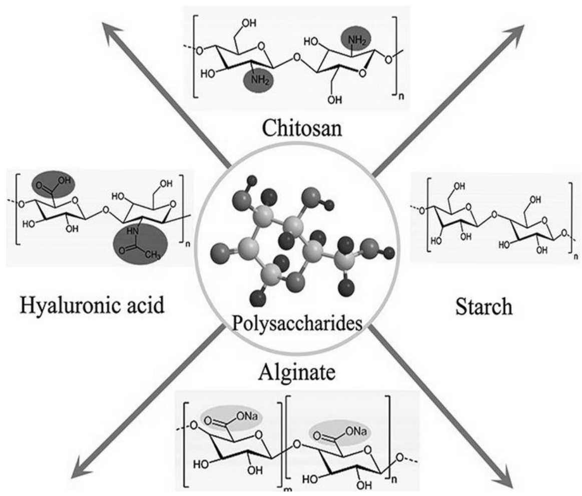

Fig. 8. The chemical structure of conventional polysaccharides (chitosan, starch, alginate and hyaluronic acid) [32]

The reported applications of functionalized polysaccharide–TiO_2 composites include photocatalysts, biomedical (wound-healing material, drug delivery systems, textile (cotton fabric self-cleaning), the polysaccharide–TiO_2 showed high biocompatibility, indicating that their use in food, pharmaceutical, and biomedical applications is safe [35–39]. TiO_2 NPs are irreversible adsorbed on the hydroxyl groups in the polysaccharide matrix [40]. In general, the polysaccharide–TiO_2 hybrid materials showed improved physicochemical properties in a TiO_2 content-dependent response. It showed antimicrobial activity against bacteria (gram-negative and gram-positive). Chitosan and TiO_2 mostly affect *S. aureus* monolayer structure, enhancing the permeability of biological membranes leading to the bacteria cell death [41]. One of the mechanisms of antibacterial action of mixtures containing chitosan, TiO_2, and/or hyaluronic acid is probably based on bacterial membrane disturbance. Authors [42] reported that TiO_2 nano-powder was uniformly dispersed into chitosan to form chitosan-TiO_2 film. Chitosan-

TiO_2 film showed enhanced hydrophilicity and better mechanical properties, possessed efficient antimicrobial activity under visible light and provoked the leakage of cellular substances. The combination of ZnO, TiO_2 and Ag NPs with chitosan not only improved antimicrobial activity, but also accelerated the wound healing process and enhanced the mechanical characteristics of wound materials [43]. However, the cytotoxicity of these composite materials to human and animal cells, especially in long time frames, is still unclear and delays their full implementation [44].

Application: Composites based on metal NPs in the structure of silica or titania in the presence of biopolymers are effective hemostatic agents with a bactericidal effect. Sodium alginate has a reducing and stabilizing effect on nanoparticles, and silica prevents agglomeration of metal NPs in the resulting composite.

It is quite difficult to satisfy the numerous target requirements for biomedical nanomaterials based on metal NPs in the composition of dispersed oxides as well as textiles and/or biopolymers ("all in one") to obtain a single universal multifunctional material that does not lose its properties during operation. It makes more sense to produce composites for purpose targeted applications, such as bactericidal and antiviral, hydrophobic coatings for laboratory surfaces, package and so on. Researches in this area are in progress.

Цільові вимоги до біомедичних наноматеріалів на основі дисперсних оксидів та текстилю, модифікованих металевими наночастинками

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У статті проаналізовано літературні дані та авторські розробки щодо технології створення терапевтичних депо у вигляді плівок, дисперсій оксидів металів, текстилю з іммобілізованими біосумісними наночастинками (НЧ) срібла у структурі SiO_2, TiO_2, бавовни, біополімерів. (альгінат, хітозан, лігнін тощо), які мають біоцидну дію, та майбутні тенденції в цій галузі. Ми та інші дослідники розробили методи синтезу фотокаталітично активних плівок TiO_2 і SiO_2, модифікованих НЧ золота/срібла/міді, придатних для медичного використання. Розроблено економічні та прості низькотемпературні способи виготовлення антимікробних текстильних виробів шляхом фото- або термічної активації та показана можливість їхнього багаторазового використання. Виробництво та використання біомедичного текстилю останнім часом орієнтується на широке використання нетоксичних біополімерів у поєднанні з текстилем. Отримано композиції на основі нанодисперсного кремнезему з полісахаридом альгінатом натрію та НЧ срібла з вираженими гемостатичними та бактерицидними властивостями. Для додаткового поглинання токсинів і очищення ран перспективним є отримання гібридного матеріалу в поєднанні з дисперсним оксидом. Створення таких універсальних багатофункціональних матеріалів передбачає їхню високу бактерицидну та противірусну дію при багаторазовому використанні. Гібридні матеріали на основі наночастинок металів у структурі носіїв різної природи у вигляді плівок і дисперсій біосумісних оксидів, біополімерів, текстилю мають захист від можливої токсичної дії наночастинок та іонів металів, здатність до самоочищення, фотокаталітичні, кровоспинні властивості, термостійкість та ін.

Матеріали на основі дисперсій Ag/SiO_2 мають високу антибактеріальну та противірусну дію (одноразове застосування). Плівки Ag/SiO_2 можуть виступати як довгострокове антибактеріальне покриття. Показано посилення антибактеріальних властивостей НЧ Ag-TiO_2 дисперсій під впливом видимого світла та фотокаталітична дія під УФ-опроміненням. Бавовна, модифікована НЧ срібла, міді, демонструє високу ефективність знищення бактерій та деяких грибів - E. coli, K. pneumoniae, E. aerogenes, P. vulgaris, S. aureus, C. albicans та ін., зі збереженням біоцидної активності після 5 циклів прання. Досліджено динаміку виходу іонів срібла з поверхні НЧ у структурі текстилю при їхньому контакті з водою протягом 72 годин та кількість необоротно зв'язаних частинок зі збереженням біоцидної дії. Модифіковані тканини мають багаторазове застосування.

Композити на основі НЧ металів у структурі кремнезему або оксиду титану в присутності біополімерів є ефективними гемостатичними засобами з бактерицидною дією. Альгінат натрію має відновлюючу і стабілізуючу дію на НЧ, а кремнезем запобігає агломерації металевих НЧ в отриманому композиті. Проте досить важко задовольнити численні цільові вимоги до біомедичних наноматеріалів на основі НЧ металів у складі дисперсних оксидів, а також текстилю та/або біополімерів («все в одному»), щоб отримати єдиний універсальний багатофункціональний матеріал, який не втратить свої властивості під час експлуатації. Доцільніше виробляти композити цільового призначення, наприклад, бактерицидні та противірусні, гідрофобні покриття для лабораторних поверхонь, упаковки тощо. Дослідження в цій області тривають.

Ключові слова*: наночастинки металу (НЧ), наночастинки оксиду металу (МеОНЧ), біополімери, колоїди, SiO_2 плівки, TiO_2 наночастинки, SiO_2 дисперсії, текстиль, бактерицидна активність, гемостатичні властивості*

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