Chemistry, Physics and Technology of Surface. 2020. V. 11. N 4. P. 508-515

UDC 544.77 + 549.057 doi: 10.15407/hftp11.04.508

O.M. Lavrynenko, M.N. Zahornyi, M.M. Bataiev, Yu.M. Bataiev, O.Yu. Pavlenko, O.A. Kornienko

UV IRRADIATION EFFECT ON PARAMAGNETIC PROPERTIES OF NANOMAGNETITE DOPED WITH Ag(I) AND Au(III) CATIONS

Frantsevych Institute of Problems of Materials Science of National Academy of Sciences of Ukraine
3 Krzhyzhanovskii Str., Kyiv, 03680, Ukraine, E-mail: alena.lavrynenko@gmail.com

Nowadays nanocomposites based on magnetite doped with noble metal cations or core&shell type nanocomposites including superparamagnetic core and precious metal shells are widely used in new kinds of biocompatible materials creation. The following structures are characterized by unique complexes of physical-chemical properties. The noble metal coatings formed on the magnetite nanoparticles surface supply their corrosive biological media stabilization and effects on electrical, magnetic, catalytic, optical properties of core&shell type nanocomposites as well. This work studies the effect of UV irradiation (253 nm) on the paramagnetic characteristics of biocompatible core&shell type nanocomposites based on magnetite and precious metals (silver, gold). Nanoparticles of magnetite and core&shell type composites Fe_3O_4&Ag^0 and Fe_3O_4&Au^0 were formed under the rotation-corrosion dispergation conditions on the steel 3 (St3) surface contacting with distilled water and aqueous solutions of silver nitrate and tetrachloroauric acid at a free flow of oxygen into the reaction zone. Solutions of precious metals contained from 0.5 to 20 mg/dm^3 of Ag(I) and Au(III) aquaforms. The composite nanoparticles were characterized using X-ray diffraction data, scanning electron microscopy and electron paramagnetic resonance spectroscopy. Because of expecting photocatalytic activity of as-prepared nanocomposites, we performed their illumination by ultraviolet irradiation. The effect of UV irradiation (253 nm) on the paramagnetic characteristics of biocompatible core&shell nanocomposites based on magnetite and precious metals (silver, gold) was studied by EPR analysis. The obtained data suggests that after UV irradiation the contribution of Fe^{2+} spins increases, the band gap for Fe_3O_4 decreases, the rate of charge redistribution at the oxide-metal interface increases, the number of spins in the composite increases. The study of the occurrence of paramagnetic centers mechanism in the nanocomposites based on magnetite and precious metals may be relevant for determining their bactericidal and photocatalytic activity. Also, such nanocomposites can be used in the creation of technical means for prevention of the spread of infectious diseases in the transport, public places, and hospitals.

Keywords*: core&shell type nanocomposites, the rotation-corrosion dispergation method, nanomagnetite, silver, gold, UV irradiation, EPR study, photocatalytic activity*

INTRODUCTION

Nowadays nanocomposites based on magnetite doped with noble metal cations are widely used to create new kinds of biocompatible materials characterized by unique complexes of physical-chemical properties [1, 2]. The coating of magnetite nanoparticles by noble metals leads to their stabilization in corrosive biological media and effects on their electrical, magnetic, catalytic properties and on unique plasmonic properties as well [3]. According to our study [4, 5], the magnetite nanoparticles doped with Ag^+ and Au^{3+} show no remanence magnetization and coercitivity.

Scientific publications analysis shows that nanoparticles of iron oxides, such as magnetite and maghemite, are already used in the drugs targeted delivery to target cells, to improve magnetic resonance imaging, tumor hyperthermia, *etc.* [6–8]. The practical usage of iron oxides and iron oxyhydroxides (*in vivo*) is associated with: increasing of the contrast in magnetic resonance imaging; repairing of the body tissue; immunological studies; detoxification of biological fluids; currying out of hyperthermia processes; performing of target drug delivery, and cell separation [9]. At the same time, there are works in which emphasis is placed onto the bactericidal and cytotoxic properties of biologically synthesized magnetite, for example [10]. However, core&shell type composites based on magnetite and precious metals, which combine the magnetic properties of the nucleus – iron oxide with optical (surface

plasmon resonance in a wide range of excitation irradiation frequencies) and catalytic properties of the reduced shell silver, platinum, palladium, are more attractive to biomedical application.

Composite nanoparticles may be formed via several chemical ways: 1. Co-precipitation of ferric and ferrous salts in weak-alkaline water medium with sequential formation of magnetite or maghemite cores and reduction of noble metal shells on their surfaces [11]; 2. Reversive micells method [12]; 3. Separate precipitation of nuclear magnetite and noble metal particles and their binding via organic substances [13].

An alternative synthesis method, when the phase formation process was carried out in the Green Rust presence as a precursor phases was described in [14, 15]. It should be noted that the morphology of the composite particles (not only the size) for various functional materials creation has an important role. From this point of view, the usage of oxygen-containing iron compounds allows us to form spherical, needle-shaped, plate-like structures. Such differences in morphology give a possibility to functionalize the particle surface easily and to change their colloid-chemical properties as well.

This work researched the UV irradiation effect (253 nm) on the paramagnetic characteristics of biocompatible core&shell type nanocomposites based on magnetite and precious metals (silver, gold).

OBJECTS AND METHODS OF THE RESEARCH

Nanoparticles of magnetite and core&shell type composites Fe_3O_4&Ag^0 and Fe_3O_4&Au^0 were formed under the rotation-corrosion dispergation conditions on the steel 3 (St3) surface contacting with distilled water and aqueous solutions of silver nitrate and $HAuCl_4$ at a free flow of oxygen into the reaction zone. Precious metals solutions contained amounts from 0.5 to 20 mg/dm^3 of noble metal aquaforms Ag(I) and Au(III)). The duration of the phase formation process was 24 h.

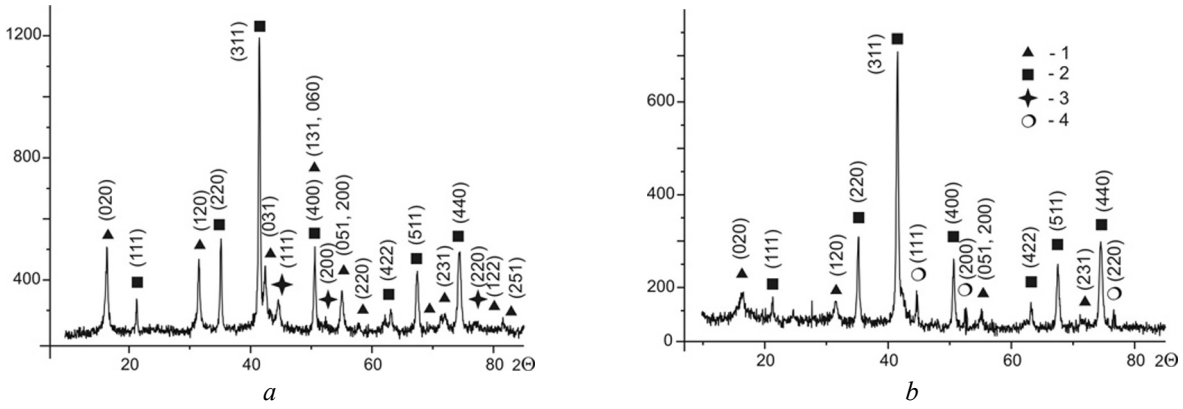
The phase composition of the nanoparticles was studied by X-ray diffraction phase analysis (X-ray diffraction) using computer-aided X-ray diffractometer (DRON – UM1) equipped with two Soller's slits and Ni filtered radiation of cobalt anode CoK_α. The rate of recording was 1°/min, and the interfacial Woolf-Bragg's angle made up 80 degrees. The coherent scattering region (CSR) was calculated according to the standard Debye-Scherrer's formula. The samples were visualized by scanning electron microscopy (SEM). Electron micrographs of the samples were recorded on a MIRA3 TESCAN scanning electron microscope. The main method of research was electronic paramagnetic resonance (EPR) using equipment model Radiopan 2547SE/X. UV irradiation of nanocomposite systems based on Fe_3O_4 was carried out by a bactericidal lamp OBB15 (9W, 253 nm) for 1 h.

RESULTS AND DISCUSSION

The composite nanoparticles characteristics. The X-ray diffraction analysis of the samples shows that the contact of St3 surface with distilled water in the open-air system leads to the formation of nanosized magnetite particles. The presence of precious metal cations in the dispersion medium, in particular, those of silver and gold, promotes their reduction on the surface of magnetite particles with the formation of shell composite structures. Fig. 1 shows typical diffractograms of the nanostructures formed on the St3 surface in the presence of silver nitrate solution (Fig. 1 *a*) and tetrachloroauric acid solution (Fig. 1 *b*). In both XRD patterns we can see the magnetite reflexes (JCPDS file No. 19-0629), and the reflexes of corresponding precious metals – silver (JCPDS file No. 04-0783) or gold (JCPDS file No. 02-1095). An additional phase is lepidocrocite (JCPDS file No. 08-0098), its formation accompanies redox processes taking place under the RCD conditions in the presence on heavy or noble metals aquaforms [16, 17]. The size of magnetite cores calculated according to the Debye-Scherrer's equation varies in the range from 20 to 24 nm.

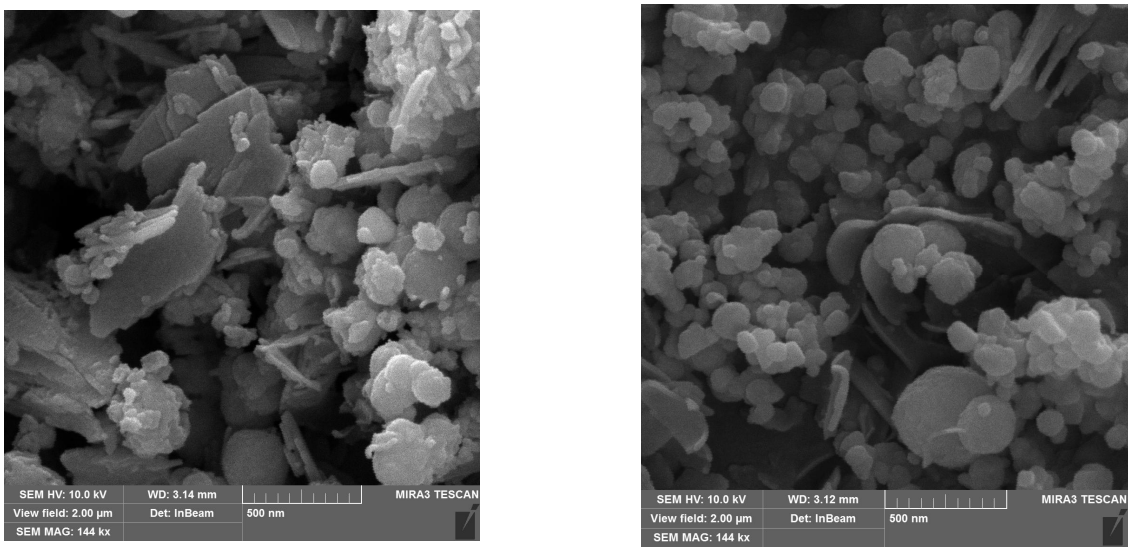
The morphology of structures is given by the SEM images in the Fig. 2. The micron sized plate-likes particles characterize the nucleation phases of Fe(II)-Fe(III) layered double hydroxides (hydroxycarbonate Green Rust) and iron oxyhydroxides (lepidocrocite with admixture of goethite). Spherical particles belong to core&shell nanocomposites based on magnetite and corresponding precious metals (silver and gold). The content of precious metals in the composite structures does not exceed 3 wt. %, what supplies the optimal properties for the composite particles susceptibility to photocatalysis and plasmon effects.

Magnetometric studies of nanocomposite structures formed on the steel surface contacting with aqueous solutions [17] indicate that, regardless of the nature of the noble cation, the magnetite particles belong to superparamagnetics with a saturation magnetization of 24 A m^2/kg (for silver shells) and 48 A m^2/kg (for gold shells). These samples show residual magnetization and coercivity. In general, the magnetism nature of such composite structures kind determines the natural properties of the magnetite nucleus, and the presence of a shell, silver in particular, usually leads to decreasing in M_s [4]. Preliminary bactericidal activity studies of core & shell type nanocomposites based on magnetite cores and silver shells showed microbicidal activity and an effect on the state of non-specific anti-infective organism resistance. The usage of the composite nanostructures Fe_3O_4&Ag^0 indicated their bactericidal activity against both gram-negative *E. Coli* and gram-positive *S. Aureus* microorganisms [18], and the silver-magnetite nanocomposites were proven to affect the state of nonspecific [19] anti-infective resistance of the body.



a *b*

Fig. 1. XRD spectra of structures formed on the steel 3 surface contacted with air and aqueous solutions: *a* – $AgNO_3$; *b* – $HAuCl_4$. The numbers indicate: *1* – lepidocrocite; *2* – magnetite; *3* – Ag; *4* – Au



a *b*

Fig. 2. SEM images of structures formed on the steel 3 surface contacted with air and aqueous solutions: *a* – $AgNO_3$; *b* – $HAuCl_4$

UV irradiation of magnetite nanoparticles and related shell composites. It is known that the ferrite nanoparticles magnetization goes according to the Curie's law. The maximum peak of the EPR spectrum obtained in the 2100 Gauss field also confirms the superparamagnetic nature of the nanocomposite samples obtained under the RCD conditions in the presence of silver- and gold-containing solutions and their higher superparamagnetic properties in the comparison with other similar materials [1, 3]. In particular, Fig. 3 shows a significant shift of the maximum (Lorentz character of the integration curves), a decrease in the intensity of the peaks (maxima), especially after UV irradiation (best seen in the Fe_3O_4&Ag^0 samples). The data obtained suggest that after UV irradiation the contribution of Fe^{2+} spins increases, the band gap for Fe_3O_4 decreases, the rate of charge redistribution at the oxide-metal interface increases, the number of spins in the composite increases. Thus, the study of the occurrence mechanism of paramagnetic centers in the structure of the core&shell type nanocomposites based on magnetite and precious metals may be relevant for determining their bactericidal and photocatalytic activity.

In the present work, we apply an EPR spectroscopy to determine the effect of UV irradiation (253 nm) on magnetization dynamics and surface magnetic properties of noble metal-bearing magnetite. In Figs. 3–4 we can see a significant shift of EPR lines of the irradiated samples to large-field area accompanied by reinforcement of ferrimagnetic properties of the nanocomposites. To compare the platinum- and palladium-contained magnetite samples, additional data were added in Fig. 4. Generally, shift intensity depends on the nature of noble metal dopants. The spin quantity of the irradiated samples decreased in all cases. The magnetization intensity under UV irradiation is also decreasing and became the same values for all investigated samples. Doping of iron oxide Fe_3O_4 with noble metals is carried out to enhance the activity during irradiation. Doping with noble metals also limits the recombination of electron-hole pairs due to the Schottky barrier at the metal-oxide semiconductor interface with the formation of a photocatalyst.

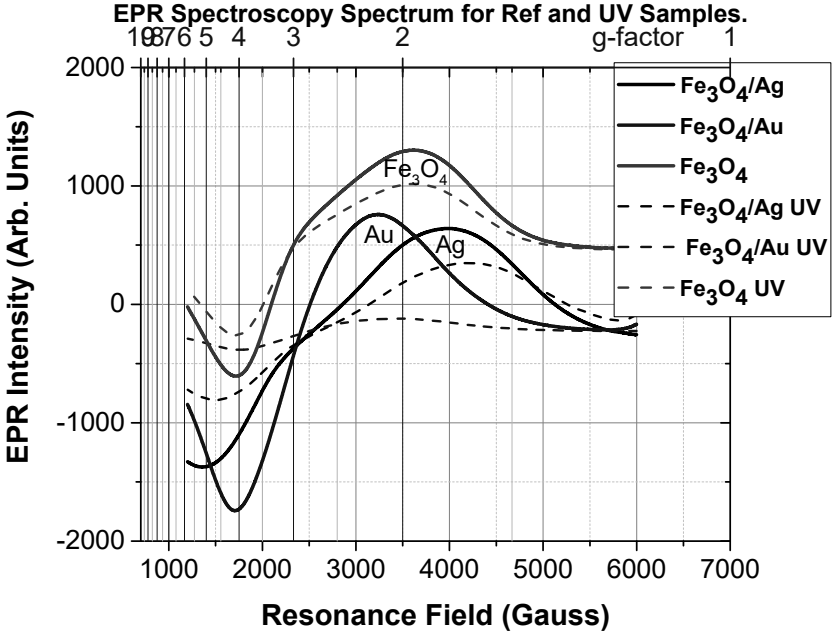


Fig. 3. Relative changes in EPR intensity spectra for magnetite doped with Ag(I), and Au(III)

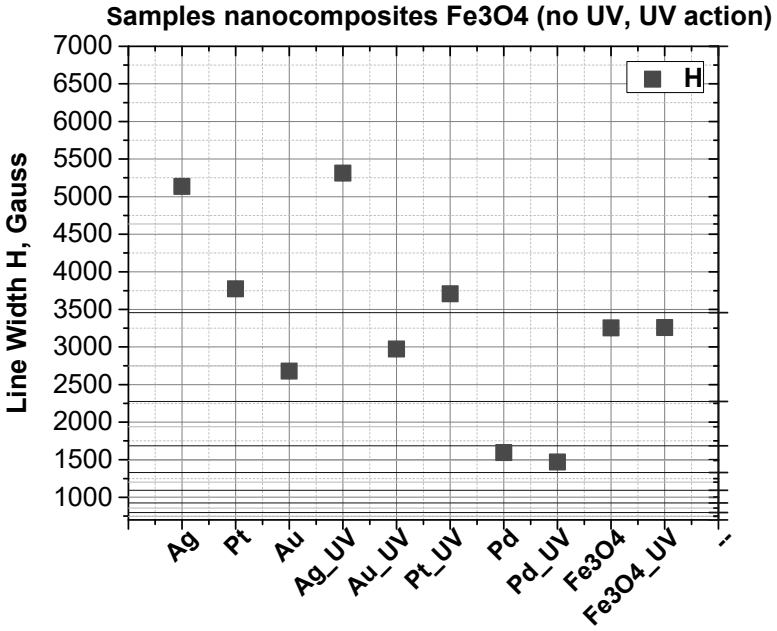


Fig. 4. Changing of the line width (H) for core&shell type nanocomposites based on Fe_3O_4 and noble metals

CONCLUSION

Today nanosized core & shell type composites containing iron oxide cores (magnetite and/or maghemite) and noble metal shells (in particular those silver or gold) are very perspective materials for biomedical applications due to combinations of magnetic, optical, and colloid-chemical properties, as well as because of the possibility to biofunctionalization of the surface of the composites.

Biocompatible core&shell type nanocomposites based on magnetite and reduced on its surface precious metals (Ag, Au) being taken as an example, a way was shown to vary the paramagnetic characteristics and the band gap of the oxide semiconductor. The presence of Fe^{2+} cations in the magnetite structure leads to the properties reducing the exchangeable reactions capability, where iron cations can be replaced by noble metal ones. The variation in the physicochemical characteristics of nanocomposites based on ferrimagnetic cores and a noble metal shells opens up great possibilities for their practical application as a platform for the development of highly effective diagnostic and therapeutic tools with selectivity at the level of individual cells and biomacromolecules.

ACKNOWLEDGEMENTS

This work was supported by the research project of NAS of Ukraine nano program “The development of photocatalytic nanocomposites for a virus inactivation in the air” (No. 40/20-H).

Вплив УФ опромінення на парамагнітні властивості наномагнетиту, допованого катіонами Ag(I) и Au(III)

О.М. Лавриненко, М.М. Загорний, М.М. Батаєв, Ю.М. Батаєв, О.Ю. Павленко, О.А. Корнієнко

Інститут проблем матеріалознавства ім. І.М. Францевича Національної академії наук України
вул. Кржижановського, 3, Київ, 03680, Україна, alena.lavrynenko@gmail.com

На сьогоднішній день нанорозмірні композити на основі магнетиту, допованого катіонами благородних металів, або оболонкові нанокомпозити, що складаються із суперпарамагнітного ядра (магнетиту або магеміту) і оболонки із благородного металу, широко використовуються для створення нових видів біосумісних матеріалів. Такі структури характеризуються унікальним комплексом фізико-хімічних властивостей. Зокрема, оболонки із благородних металів, сформовані на поверхні наночастинок магнетиту, забезпечують їхню стійкість в агресивних біологічних середовищах, а також впливають на їхні електричні, магнітні, каталітичні, оптичні властивості. В роботі проведено вивчення впливу ультрафіолетового випромінювання (253 нм) на парамагнітні характеристики біосумісних оболонкових нанокомпозитів. Наночастки композитів Fe_3O_4&Ag^0 і Fe_3O_4&Au^0 були отримані методом ротаційно-корозійного диспергування. Формування структур проходило на поверхні сталі 3 (Ст3), яка контактувала з дистильованою водою і водними розчинами нітрату срібла і золотохлористоводневої кислоти при вільному доступі кисню в зону реакції. Розчини благородних металів містили від 0,5 до 20 мг/дм^3 аквaформ Ag(I) і Au(III). Отримані наночастинки були охарактеризовані методом рентгенофазового аналізу і скануючої електронної мікроскопії. Для виявлення очікуваних фотокаталітичних властивостей частинки композитів підлягали дії ультрафіолетового опромінення. Вплив УФ-випромінювання (253 нм) на парамагнітні характеристики нанокомпозитів Fe_3O_4&Ag^0 и Fe_3O_4&Au^0 було вивчено методом ЕПР. Отримані дані свідчать про те, що після УФ-опромінення збільшувалися: швидкість перерозподілу заряду на поверхні поділу оксид-метал, кількість і внесок спинів Fe^{2+}, при цьому ширина забороненої зони для Fe_3O_4 зменшувалася. Вивчення механізму виникнення парамагнітних центрів в нанокомпозитах на основі магнетиту і благородних металів може бути актуальним для виявлення їхньої бактерицидної і фотокаталітичної активності. В цілому, оболонкові нанокомпозити можуть бути використані при створенні технічних засобів бактерицидної та антивірусної дії, призначених для запобігання поширенню інфекційних захворювань в замкнутому просторі (на транспорті, в громадських місцях, лікарнях).

***Ключові слова**: оболонкові нанокомпозити, ротаційно-корозійне диспергування, наномагнетіт, срібло, золото, УФ випромінювання, ЕПР дослідження*

Влияние УФ облучения на парамагнитные свойства наномагнетита, допированного катионами Ag(I) и Au(III)

Е.Н. Лавриненко, М.Н. Загорный, Н.Н. Батаев, Ю.Н. Батаев, О.Ю. Павленко, О.А. Корниенко

Институт проблем материаловедения им. И.Н. Францевича Национальной академии наук Украины
ул. Кржижановского, 3, Киев, 03680, Украина, alena.lavrynenko@gmail.com

На сегодняшний день наноразмерные композиты на основе магнетита, допированного катионами благородных металлов, или нанокомпозиты ядро-оболочка, состоящие из суперпарамагнитного ядра (магнетита или маггемита) и оболочки из благородного металла, широко используются для создания новых видов биосовместимых материалов. Такие структуры характеризуются уникальным комплексом физико-химических свойств. В частности, оболочки из благородных металлов, сформированные на поверхности наночастиц магнетита, обеспечивают их устойчивость в агрессивных биологических средах, а также влияют на их электрические, магнитные, каталитические, оптические свойства. В данной работе изучено влияние ультрафиолетового излучения (253 нм) на парамагнитные характеристики биосовместимых нанокомпозитов. Наночастицы композитов Fe_3O_4&Ag^0 и Fe_3O_4&Au^0 были получены методом ротационно-коррозионного диспергирования. Формирование структур проходило на поверхности стали 3 (Ст3), контактирующей с дистиллированной водой и водными растворами нитрата серебра и

золотохлористоводородной кислоты при свободном доступе кислорода в зону реакции. Растворы благородных металлов содержали от 0.5 до 20 мг/дм³ акваформ Ag(I) и Au(III). Полученные наночастицы были охарактеризованы методом рентгенофазового анализа и сканирующей электронной микроскопии. Для выявления ожидаемых фотокаталитических свойств частицы композитов подвергались действию ультрафиолетового облучения. Влияние УФ-излучения (253 нм) на парамагнитные характеристики нанокомпозитов Fe_3O_4&Ag^0 и Fe_3O_4&Au^0 было изучено методом ЭПР. Полученные данные свидетельствуют о том, что после УФ-облучения увеличивались: скорость перераспределения заряда на границе раздела оксид-металл, число и вклад спинов Fe^{2+}, при этом ширина запрещенной зоны для Fe_3O_4 уменьшалась. Изучение механизма возникновения парамагнитных центров в нанокомпозитах на основе магнетита и благородных металлов может быть актуальным для выявления их бактерицидной и фотокаталитической активности. В целом, полученные нанокомпозиты могут быть использованы при создании технических средств бактерицидного и антивирусного действия, предназначенных для предотвращения распространения инфекционных заболеваний в замкнутом пространстве (на транспорте, в общественных местах, больницах).

***Ключевые слова**: нанокомпозиты ядро-оболочка, ротационно-коррозионное диспергирование, наномагнетит, серебро, золото, УФ излучение, ЭПР исследования*

REFERENCES

1. Zhichuan X., Yanglong H., Shouheng S. Magnetic Core/Shell Fe_3O_4/Au and Fe_3O_4/Au/Ag Nanoparticles with Tunable Plasmonic Properties. *J. Am. Chem. Soc.* 2007. **129**(28): 8698.
2. Lavrynenko O.M., Dolynskyi G.A. Nanoscale Core & Shell Composites (Iron Oxide – Noble Metal): Preparation, Structure, Properties, Prospects for Biomedical Applications. *Material Science of Nanostructures*. 2011. **3**: 3. [in Russian].
3. Mahmood A., Ramay Sh.M., Al-Zaghayer Y.S., Al-Hazaa A.N., Al-Masary W.A., Atiq Sh. Au doping effect on the electrical and magnetic properties of Fe_3O_4 nanoparticles. *Mod. Phys. Lett. B.* 2015. **29**(33): 1550213.
4. Lavrynenko O.M. Physicochemical properties of the $FeFe_2O_4$&Ag^0 nanocomposites formed on the steel surface contacting with $AgNO_3$ water solutions in open-air system. *Nano Studies*. 2012. **5**: 27.
5. Lavrynenko O.M., Dudchenko N.O., Shchukin Yu.S., Brik O.B. Magnetic properties of nanoparticles formed on the steel surface contacting with aurum-bearing water solutions. In: *Proceedings of the IEEE 8th International Conference Nanomaterials: Applications & Properties*. 2018. **7**(1): 01SPN17.
6. Liu E., Zhang M., Cui H., Gong J., Huang Y., Wang J., Yang V.C. Tat-functionalized Ag-Fe_3O_4nano-composites as tissue-penetrating vehicles for tumor magnetic targeting and drug delivery. *Acta Pharmaceutica Sinica B.* 2018. **8**(6): 956.
7. Mamani J.B., Gamarra L.F., de Souza Brito G.E. Synthesis and Characterization of Fe_3O_4 Nanoparticles with Perspectives in Biomedical Applications. *Mater. Res.* 2014. **17**(3): 542.
8. Kim J., Piao Y., Hyeon T. Multifunctional nanostructured materials for multimodal imaging, and simultaneous imaging and therapy. *Chem. Soc. Rev.* 2009. **38**(2): 372.
9. Gupta A.K., Gupta M. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials*. 2005. **26**(18): 3995.
10. Sathishkumar G., Logeshwaran V., Sarathbabu S., Jha P.K., Jeyaraj M., Rajkuberan C., Senthilkumar N., Sivaramakrishnan S. Green synthesis of magnetic Fe_3O_4 nanoparticles using Couroupita guianensis Aubl. fruit extract for their antibacterial and cytotoxicity activities. *Artif. Cells Nanomed. Biotechnol*. 2018. **46**(3): 589.
11. Pham H.T., Cao C., Sim S.J. Application of citrate stabilized gold-coated ferric oxide composite nanoparticles for biological separations. *J. Magn. Magn. Mater.* 2008. **320**(15): 2049.
12. Park S.-E., Lee J.-W., Haam S.-J., Lee S.-W. Fabrication of Double-Doped Magnetic Silica Nanospheres and Deposition of Thin Gold Layer. *Bulletin - Korean Chemical Society.* 2009. **30**(4): 869.
13. Caruntu D., Cushing B.L., Caruntu G., O'Connor C.J. Attachment of gold nanograins onto colloidal magnetite nanocrystals. *Chem. Mater*. 2005. **17**(13): 3398.
14. Ayadi S., Perca C., Legrand L. New one-pot synthesis of Au and Ag nanoparticles using green rust reactive particle as a micro-reactor. *Nanoscale Res. Lett*. 2013. **8**(1): 95.
15. Lavrynenko O.M., Vember V.V., Shchukin Yu.S. Formation of Core&Shell Type Nanocomposites Based on the Fe(II)-Fe(III) Layered Double Hydroxides. *Visnyk NTTU «KPI im. Ihoria Sikorskoho». Seriia: Khimichna inzheneriia, ekolohiia ta resursozberezhennia*. 2019. **1**(18): 86. [in Ukrainian].

16. Lavrynenko O.M., Pavlenko O.Yu., Shchukin Yu.S. Characteristic of the Nanoparticles Formed on the Carbon Steel Surface Contacting with 3d-Metal Water Salt Solutions in the Open-Air System. *Nanoscale Res. Lett*. 2016. **11**(1): 67.
17. Lavrynenko O.M., Pavlenko O.Yu., Shchukin Yu.S., Dudchenko N.O., Brik A.B., Antonenko T.S. Chapter 28. Characteristics of Nanocomposites Formed on the Steel Surface Contacting with Precious Metal Solutions. *Springer Proceedings in Physics Microstructure and Properties of Micro- and Nanoscale Materials, Films, and Coatings* (NAP 2019). 2020. P. 297.
18. Lavrynenko O.M., Dolynskyi G.A., Nosov V.V., Kislukhina M.O. Antimicrobial properties of $FeFe_2O_4$ & Ag^0 nanocomposites. In: *Abstracts of 3rd International Conference "Nanotechnologies"* (October 20–24, 2014, Tbilisi, Georgia, Nano–2014). P. 75.
19. Dolynskyi G.A., Lavrynenko O.M., Nosov V.V. Antiinflammatory Properties of Nanocomposite $FeFe_2O_4$&Ag^0 in Experimental Peritonitis. *Odeskyi medychnyi zhurnal*. 2014. **2**(141): 10. [in Russian].

Received 03.09.2020, accepted 25.11.2020