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НАУКА, НОВЫЕ ТЕХНОЛОГИИ И ИННОВАЦИИ КЫРГЫЗСТАНА, № 4, 2020

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ДЕИОНИЗАЦИЯЛАНГАН СУУДА ИМПУЛЬСТУК ПЛАЗМА АРКЫЛУУ АЛЫНГАН МАГНЕТИТ НАНОБӨЛҮКЧӨЛӨРҮ

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НАНОЧАСТИЦЫ МАГНЕТИТА, ПОЛУЧЕННЫЕ В ИМПУЛЬСНОЙ ПЛАЗМЕ В ДЕИОНИЗИРОВАННОЙ ВОДЕ

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MAGNETITE NANOPARTICLES OBTAINED BY THE PULSED PLASMA IN DEIONIZED WATER

УДК: 620.3

Бул макалада темир электроддорун иондоштурулган сууда импульстук плазмада чачуу жолу менен алынган магнетит нанобөлүкчөлөрүн изилдөө натыйжалары көрсөтүлгөн. Авторлор эксперименталдык жол менен метастабильдүү системалардын (бул учурда алтын наноэритмеси) жогорку сезгичтиги реагенттерге тийгизилген тизилиш калыбына келтирүү процессинин натыйжасына таасирин тийгизет деп ырасташкан. Бул химиялык да, биологиялык дагы, нанобъекттердин активдүүлүгүнүн жогорулагандыгын билдирет. Импульстуу плазмада алынган нанобөлүкчөлөр биологиялык активдүү нанопрепараттар үчүн прекурсор катары колдонулушу мүмкүн. Гантель формасындагы Fe_3O_4/Au нанобөлүкчөлөрү синтезделди, алар клеткаларды жана белокторду магниттик бөлүү үчүн, биосенсорлорду жана биофункционалдык нанозондорду, бактериялык инфекцияларга жана ракка каршы агенттерди өндүрүүдө, ошондой эле магниттик-резонанстык диагностикада колдонулушу мүмкүн. Алгачкы натыйжалар биз синтездеген Fe_3O_4/Au нанобөлүкчөлөрүнүн адамдын клеткалары үчүн цитотоксикалдуулугу таза Fe_3O_4 нанобөлүкчөлөрүнүн цитотоксикалдуулугунан төмөн деген тыянак чыгарууга мүмкүндүк берет.

Негизги сөздөр: *нанобөлүкчөлөр, магнетит, пульсацияланган плазма, иондоштурулган суу, медицина, CPyBr суу өткөргүч, магниттик нанобөлүкчөлөр.*

В данной статье показаны результаты исследований наночастиц магнетита, полученных диспергированием железных электродов в импульсной плазме в деионизированной воде. Экспериментально подтверджена гипотеза авторов о повышенной чувствительности метастабильных систем (в данном случае нанораствора золота) о том, что даже последовательность воздействия реагентов влияет на результат процесса восстановления. Это свидетельствует о повышенной активности нанообъектов, как химической, так и биологической. Наночастицы, полученные в импульсной плазме, могут быть использованы в качестве предшественников для биологически активных нанопрепаратов. Синтезированы гантелевидные наночастицы Fe_3O_4 / Au, которые могут найти применение для магнитного разделения клеток и белков, в производстве биосенсоров и биофункциональных нанозондов, агентов против бактериальных инфекций и рака, а также для магнитно-резонансной диагностики. Предварительные результаты позволяют сделать вывод, что цитотоксичность для клеток человека наночастиц Fe_3O_4/Au, синтезированных нашим методом, ниже цитотоксичности чистых наночастиц Fe_3O_4.

Ключевые слова: *наночастицы, магнетит, импульсная плазма, деионизированная вода, медицина, суфрактант CpyBr, магнитные наночастицы.*

This article shows the results of studies of magnetite nanoparticles obtained by dispersing iron electrodes in a pulsed plasma in deionized water. It was experimentally proved that the authors hypotheses about the increased sensitivity of metastable systems (in the case of nano-soluble gold) that even exposure to reagents affects the result of the recovery process. This indicates a high activity of nano objects, both established and biological. Nanoparticles derived by pulse plasma can be used as precursors for biologically active nanomedicines. Dumbbell-shaped Fe_3O_4/Au nanoparticles have been synthesized, which can be used for magnetic separation of cells and proteins, in the production of biosensors and biofunctional nanoprobes, agents against bacterial infections and cancer, as well as for magnetic resonance diagnostics. Preliminary results allow us to conclude that the cytotoxicity for human cells of Fe_3O_4/Au nanoparticles synthesized by our method is lower than the cytotoxicity of pure Fe_3O_4 nanoparticles.

Key words: *nanoparticles, magnetite, pulsed plasma, deionized water, medicine, CPyBr sufractant, magnetic nanoparticles.*

1. Introduction. Recently, the use of magnetite nanoparticles in medicine has been of particular interest [1-4]. It was shown that the total sorption surface area of magnetite nanoparticles with a size of 6-12 nm is 800-1200 m^2/g, and the magnetic field induced by each particle is 300-400 kA/m [5]. Magnetite nanoparticles can be used in the transport of hydrophobic drugs [6], in the treatment of cancer, and in intracellular hyperthermia. It was

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established that Fe_3O_4 nanoparticles possess good adsorption ability to antigens [7] and viruses. The sorption activity of magnetite nanoparticles with respect to salts of heavy metals, nitrates, phenol and inertness with respect to the main electrolytes of blood plasma was demonstrated, which makes it possible to use them for purification of biological body fluids, as well as drinking water [8]. There are physical and chemical methods for synthesis of magnetite nanoparticles such as condensation [9], nanodispersion methods of compact materials related to physical effects on a solid substance nanostructuring. Chemical methods include thermolysis of metal-containing compounds, ultrasonic decomposition of metal-containing compounds, and the sol-gel method [10]. For mechanical nanodispersion using mills of various designs, there is a limit to achieve a narrow-sized nanoparticle size. Electrochemical dispersion in this sense seems more interesting, because it allows more accurate control of energy supplied to the surface of a solid, along with the dispersion of resulting products.

In this work we are reporting magnetite nanoparticles obtained using pulsed plasma created in deionized water between two metal iron electrodes. Single pulse discharge was created in extreme conditions and allowed nanoparticles to form a high specific surface area and a high sorption activity. It should be emphasized, that the energy supplied to electrodes during pulsed plasma resulting in an energy-saturated system formation. A high pressure and temperature gradient allows in stabilization and preservation of formed nanoparticles. Advantage of our method is the high efficiency and simplicity of experiment for synthesis of magnetite nanoparticles.

2. Research materials and methods. Dispersion of the iron electrodes (ALDRICH products) with a purity of 99.98% was carried out in 0.1% deionized water containing solution of surfactant CPyBr. After experiment the black fine precipitate was separated from an aqueous medium by centrifugation, and washed repeatedly with deionized water and ethanol mixture, then dried at room temperature. Yellow color aqueous solution of gold nanoparticles with concentration of 1% was obtained similarly to the work [11]. An aqueous solution of bulk $HAuCl_4$ was prepared by dissolving the reactive hydrogen tetrachloroaurate. We carried out an adsorption of cationic surfactant CPyBr on the surface of freshly formed magnetite nanoparticles in order to stabilize them and prevent from oxidation and transition to Fe_2O_3 due to their hydrophobization on the nanoparticles surface.

3. Results and discussions. At low concentrations of the surfactant CPyBr, only pyridinium ions were interacted with the negative surface centers due to electrostatic properties. In this case, horizontal orientation of surfactant molecules provided a fairly high hydrophobization. With an increase in the concentration of surfactant CPyBr, formation of a second layer of molecules was observed. In this case, an adsorption centers are the hydrocarbon radicals of the first layer. Due to hydrophobic interactions between alkyl chains of ions and adsorbate molecules, the polar groups were oriented into aqueous phase, and the surface becomes hydrophilic. Hydrophobization of the magnetite nanoparticles surface is possible only under use of CPyBr surfactant at low concentrations [12], i.e. our experimental data is in a good agreement with the theoretical concept.

3.1. X-ray diffraction analysis. The X-ray diffraction pattern of the iron dispersion product shown in the Fig. 1 was obtained by the powder method on a PANalytical X-ray apparatus with a PIXcel 3D detector with CuKα radiation (nanobiomedical center of the Adam Mickiewicz University, Poland). Fine powders were suspended in ethanol by ultrasonic mixing. Suspensions were placed on a copper substrate, dried in air at room temperature, and then analyzed using a JEOL-120FX transmission electron microscope (at Nanobiomedical center of Adam Mickiewicz University, Poznan, Poland). The diffraction pattern analysis in the Figure 1 is establishing that, when iron was dispersed in a 0.1% aqueous solution of surfactant CPyBr, two phases were formed: 1) Fe_3O_4 nanoparticles (black indices) - 89%; and 2) Fe nanoparticles (red indices) - 11%. These phases were separated by centrifugation method at a centrifuge speed of 3000 rpm.

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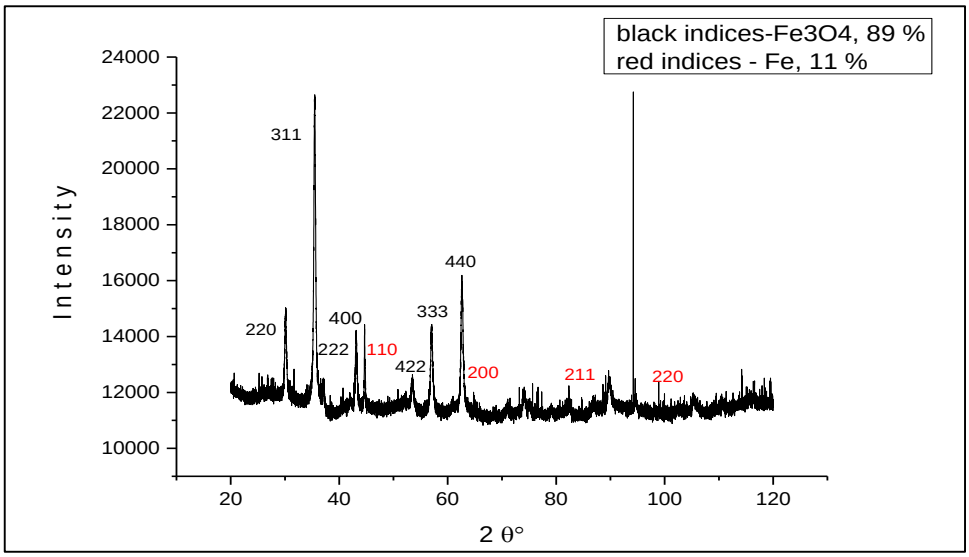

Figure 1. X-ray diffraction pattern of the iron dispersion product obtained in the 0.1% aqueous solution of surfactant CPyBr.

3.2. Transmission Electron Microscopy analyses. Transmission Electron Microscopy (TEM) analyses were used for observation and imaging of the obtained magnetite particles as shown in the Figure 2. The hexagonal phase nanoparticles of magnetite with sizes from 20 to 85 nm are clearly visible in the image. The structure of magnetite nanoparticles have cubic phase with cell parameters of a=0.8387 nm, and the space group of Fd3m.

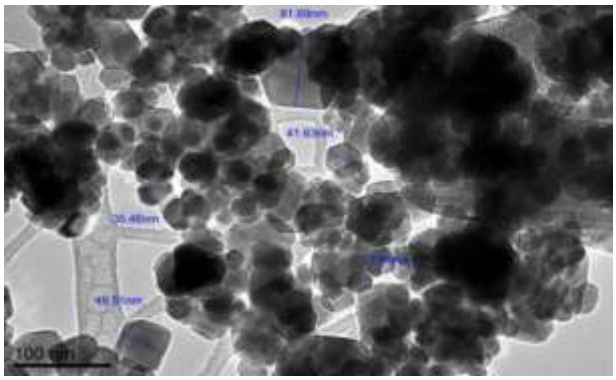

Figure 2. TEM image of Fe_3O_4 nanoparticles obtained by IPL method.

Nowadays, Fe_3O_4/Au nanoparticles are considering as applicable for magnetic separation of cells and proteins [13], the manufacture of biosensors and bio-functional nanoprobes, photothermoconotherapy agents for bacterial infections and cancer, as well as magnetic resonance diagnostics [14]. High temperature synthesis in organic media, sonolysis, synthesis with gold nuclei, and reduction of gold in aqueous solutions with hydroxylamine, glucose, sodium citrate, and formaldehyde [15] are used to produce magnetic nanoparticles with a gold shell. For the synthesis of Fe_3O_4/Au nanoparticles, we used magnetite nanoparticles obtained in 0.1% surfactant CPyBr solution a gold nanosolution and a 0.1% sodium citrate solution as a reducing agent. Figure 3 is showing TEM image of a samples obtained by processing of 0.1 g magnetite nanoparticles with solution of sodium citrate, and with a gold nanosolution. Dumbbell-shaped Fe_3O_4/Au nanoparticles were found (shown by arrows in the Figure 3 a, b). Under the influence of x-ray radiation, gold nanoparticles were melted and combined together, by forming large gold nanoparticles (Figure 3c).

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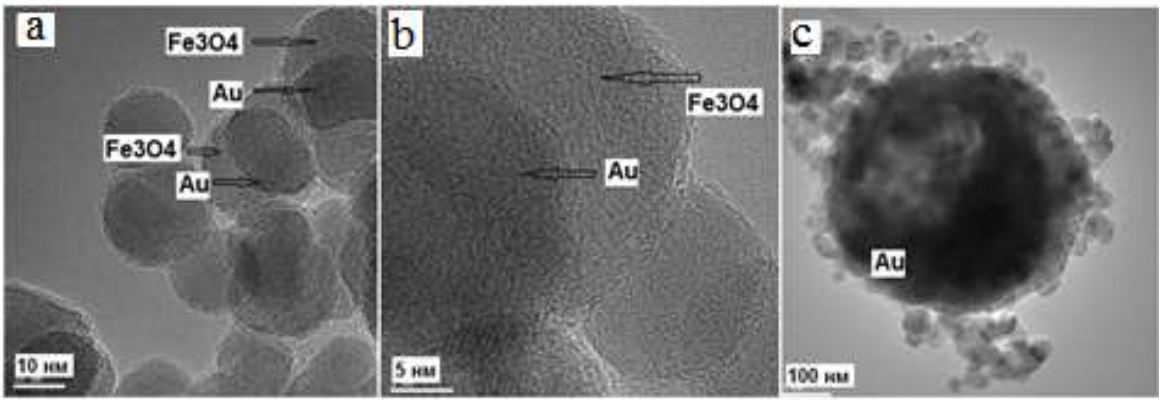

Figure 3. TEM images of the dumbbell-shaped Fe_3O_4/Au nanoparticles obtained from magnetite.

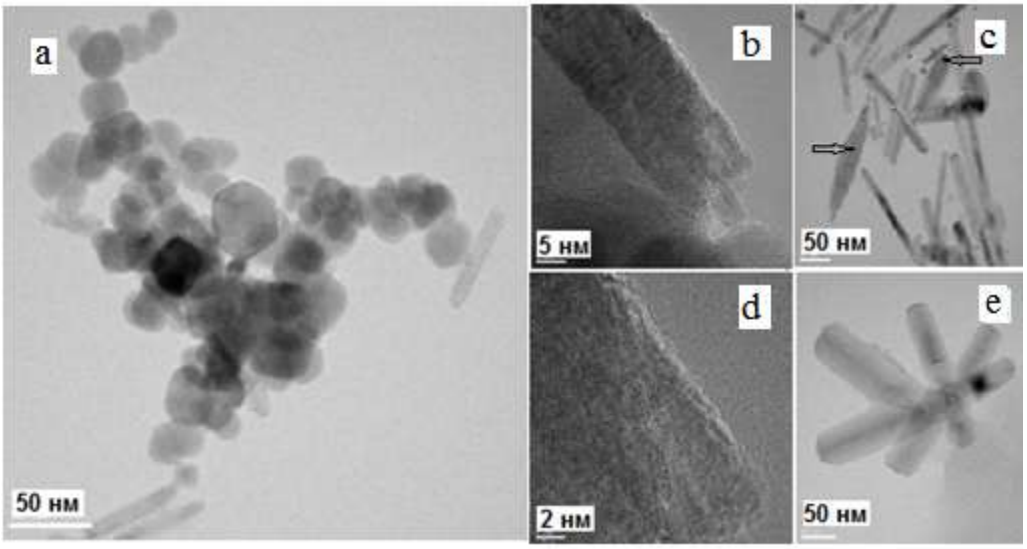

Figure 4. Reaction results of sodium citrate nanosolution and magnetite nanoparticles formed by IPL method.

It is clearly seen that the shapes of magnetite nanoparticles have not changed in the Figure 4a, while in the first experiment the dumbbell-shaped nanoparticles based on spherical magnetite and gold nanoparticles were formed. Gold nanoparticles with the shape of nanoband (Figure 4b), fusiform gold nanoparticles with spindle-shape, Figure 4c shown by arrows), nanogapes (Figure 4e) were sedimented separately from the magnetite nanoparticles. An individual gold nanoparticle is shown in the Figure 4d.

Conclusion. Our experiments confirmed the opinion of authors about increased sensitivity of metastable systems, that the sequence of reagents exposure affects the result of the recovery process. This is indicating hyperactivity of nanomedia, both chemical and biological. Nanoparticles obtained by the IPL method can be used as precursors for biologically active nanomedicines.

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