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PREPARATION AND CHARACTERISTICS OF BIMETALCARBONIC NANOCOMPOSITE FeCu@C

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Abstract

A simple and materially beneficial method for the synthesis of a mixed iron-copper nanocomposite in a carbon matrix from synthetic humic substances has been developed. The method is based on the pyrolysis of mixture of ferum and cuprum humates in a hydrogen atmosphere at 800–900 °C. The characterization of the iron-copper nanocomposite was carried out by X-ray diffraction, scanning electron microscopy, X-ray fluorescence analysis, and voltammetric method. It was found that the synthesized nanocomposite is metal formations up to 700–1000 nm in size, located on the surface of a carbon matrix, which, according to X-ray diffraction data, is amorphous. Energy dispersive X-ray spectroscopy showed that the spherical formations are composed mainly of copper. No peaks of the bcc iron phase were found in the diffraction pattern of the sample. However, the data of X-ray fluorescence spectroscopy confirm the presence of both elements in the composition of the composite, and the execute voltammetric study convincingly proves that these elements are there in a zero-valent state. It was found that the iron-copper nanocomposite is characterized by good electrical conductivity, but the absence of ferromagnetic properties due to the fact that iron forms a common fcc crystal lattice with copper.

Keywords: nano-structures; iron-copper nanocomposites; synthetic humic substances.

ОДЕРЖАННЯ ТА ХАРАКТЕРИСТИКА БІМЕТАЛКАРБОНОВОГО НАНОКОМПЗИТУ FeCu@C

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Анотація

Розроблено простий та матеріально вигідний метод синтезу змішаного залізо-мідного нанокompозиту в карбоновій матриці з синтетичних гумінових речовин. Метод базується на піролізі суміші синтетичних гуматів феруму та купруму у водневій атмосфері при температурі 800–900 °C. Характеризацію залізо-мідного нанокompозиту здійснювали методом рентгенівської дифракції, скануючої електронної мікроскопії, рентгенофлуоресцентного аналізу, вольтамперометричного методу. Встановлено, що синтезований нанокompозит являє собою металічні утворення розміром до 700–1000 нм, розташованих на поверхні карбонової матриці, яка за даними рентгенівської дифракції є аморфною. Енергодисперсійна рентгенівська спектроскопія показала, що сферичні утворення складаються, в основному, з міді. На дифрактограмі зразка отриманого нанокompозиту піків ОЦК фази заліза не виявлено. Однак, дані рентгено-флуоресцентної спектроскопії підтверджують наявність у складі композиту обох елементів, а проведене вольтамперометричне дослідження переконливо доводить, що ці елементи знаходяться там у нуль-валентному стані. Виявлено, що залізо-мідний нанокompозит характеризується хорошою електропровідністю, але відсутністю феромагнітних властивостей, через те, що залізо формує спільну з міддю ГЦК кристалічну решітку.

Ключові слова: наноструктури; залізо-мідні нанокompозити; синтетичні гумінові речовини.

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Introduction

In modern fundamental science, the development of the basics for the synthesis of new promising materials with specified physicochemical properties remains the key task of most scientists in the world. In recent decades, special attention has been paid to methods for the preparation and study of nanoscale materials, one of which are metal-carbon nanosystems [1–3]. Their properties are determined not only by the size and composition of metal nanoparticles, but also by the nature of the carbon matrix. In this regard, these materials are capable of exhibiting unique physicochemical properties and, as a consequence, have a wide potential spectrum of their practical application [4–7].

One of the most effective ways to obtain metal-carbon nanocomposites from the point of view of efficiency and simplicity of hardware design is the method of simultaneous synthesis of reduced metal nanoparticles and the formation of a carbon carrier by thermal decomposition of carbon-containing substances, including metal salts [8]. A promising but little-studied area is the use of natural and synthetic humic substances as sources of carbon in the synthesis of metal-carbon nanocomposites [10–12]. However, synthetic humic substances are characterized by a disorder of structure [12; 13], which is expressed in the absence of peaks on the diffraction patterns, and we can assume that the carbon matrix after pyrolysis will retain the amorphous structure of the precursor.

Recently, the attention of researchers is drawn to metal-carbon nanocomposites which include two or more metals [14; 15]. Of particular interest are those that contain metals that differ significantly in their catalytic, electrochemical or magnetic properties. An example of such a pair of metals is copper and iron, the first of these metals is diamagnetic while the second is ferromagnetic. Also known is the property of iron to catalyze the transformation of the carbon matrix with the formation of crystalline carbon nanoforms, in particular multiwall carbon nanotubes.

In the scientific literature there are a relatively few publications on the thermal synthesis of such nanocomposites [16; 17] and generally a small number of papers on the use of synthetic humic substances as a source of carbon [18; 19].

Based on this, the aim of this work was to develop a simple and cost-effective method for the synthesis of bimetallic carbon nanocomposite by pyrolysis in a hydrogen atmosphere of a mixture of humates Fe and Cu. The use of

synthetic humic acid, which contains the heteroelement Nitrogen, will allow to obtain a carbon matrix doped with atoms of this element. Such nanocomposites are intensively studied for the possibility of their use as a material for electrodes of fuel cells. Controlling the introduction of the amount of metal salts into the synthetic humic substance, as well as their ratio, allows you to control the phase composition and dispersion of the forming nanoparticles of the solid solution and, as a consequence, their properties.

Experimental part

Synthetic humic acids were obtained according to the method described in [20], which included two steps: 1) preparation of nitrogen-containing oligomer by condensation of hexamethylenetetramine with pyrocatechol and 2) oxidation of the product with molecular oxygen in alkaline medium.

Synthesis of monometallic nanocomposites (iron-carbon and copper-carbon) was carried out in 2 stages. First, iron(III) humate (or copper(II) humate) was obtained by adding an excess of $\text{Fe}(\text{NO}_3)_3$ (or $\text{Cu}(\text{NO}_3)_2$) solution to sodium humate solution. The resulting precipitate was washed by decantation, vacuum filtered, and dried at 100°C . At the next stage, ferum(III) humate (or cuprum(II) humate) was pyrolyzed in a hydrogen atmosphere at 800°C for 1 hour.

The synthesis of the iron-copper nanocomposite involved the production of copper and iron humates by adding an excess of a solution of a metal salt to the sodium humate solution ($\text{Cu}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$). After draining the mother liquor, the precipitate was dispersed in 100 ml of distilled water, combining suspensions of Cu and Fe humates, stirred at high speed with a magnetic stirrer for one hour, then filtered under vacuum, washed on a Buchner funnel and dried at $t = 100^\circ\text{C}$. The resulting mixture of humates of copper and iron was subjected to pyrolysis in a hydrogen atmosphere. Furnace gases during pyrolysis were tested for ammonia and carbon (IV) oxide by passing through a saturated solution of calcium hydroxide and Nessler's reagent solution. The time required for the practical complete separation of these substances was about one hour in a hydrogen atmosphere at a temperature of 800°C . Heating the furnace to work temperature and cooling it to room temperature, also took place when passing hydrogen. Since hydrogen passed through a desiccant with concentrated sulfuric acid before being fed into

the furnace, the appearance of water condensate on the cold part of the tube at the outlet of the furnace also indicates the presence of water in the furnace gases.

X-ray diffraction patterns were taken on a DRON-2 diffractometer using $\text{FeK}\alpha$ radiation with a wavelength $\lambda = 0.19359$ nm. Spectra of X-ray fluorescence analysis were recorded on a device manufactured by Spectroscan with an energy-dispersion detector. Elvax software was used to visualize the spectrum.

Voltammetric studies were performed on a PA2 polarograph at a potential scan rate of 50 mV/s. The composite was applied to the platinum microelectrode by abrasive method (rubbing).

Results and discussion

Obtaining a mixed humate of two metals containing metals in a given molar ratio is not an easy task, due to the different bond strength of metal cations. The solution to this problem is to prepare a close mechanical mixture of two humates. The method developed in our laboratory involves the separate precipitation of each humate by adding to the solution of sodium humate excess metal salt solution. The resulting mixture of iron and copper humates was subjected to pyrolysis in a hydrogen atmosphere.

The diffraction pattern of the nanocomposite powder obtained in $\text{FeK}\alpha$ radiation is shown in Fig. 1. Comparison of the angular location of reflexes on the diffraction pattern with the values of angles given on PDF database cards [21], leads to the conclusion that the nanocomposite contains only fcc phase, which in the location of reflexes may correspond to metallic copper [22].

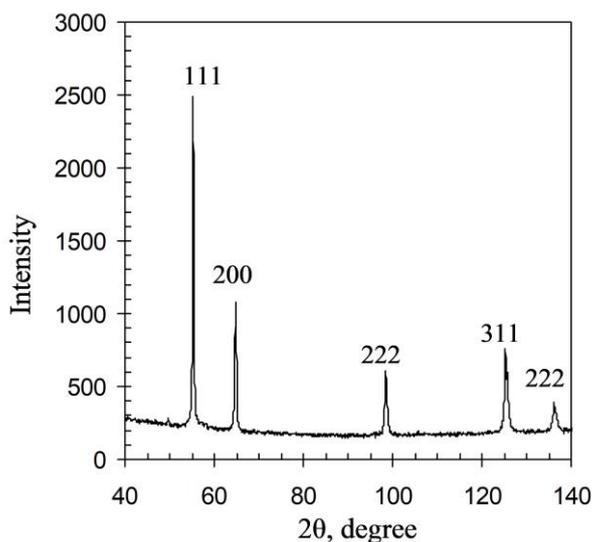


Fig. 1. Diffraction pattern of FeCu@C nanocomposite

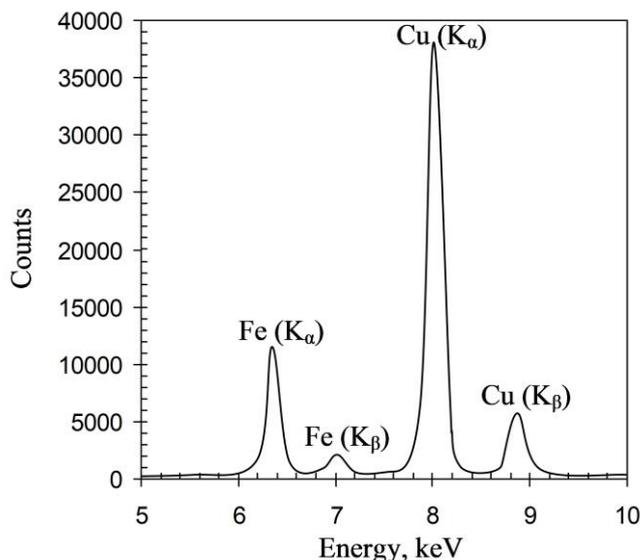


Fig. 2. X-ray fluorescence spectra of iron-copper nanocomposite

It is known that copper is characterized by fcc crystal lattice, while iron is characterized by a body-centered cubic lattice (bcc) [22].

On the other hand, the data of X-ray fluorescence spectroscopy (Fig. 2) show the presence of both elements in the composite, and

the voltammetric study convincingly proves that these elements are there in the zero-valence state. Cyclic voltammograms of separate nanocomposites of iron and copper in the carbon matrix of synthetic humic substances and iron-copper nanocomposite are shown in Fig. 3 (a, b).

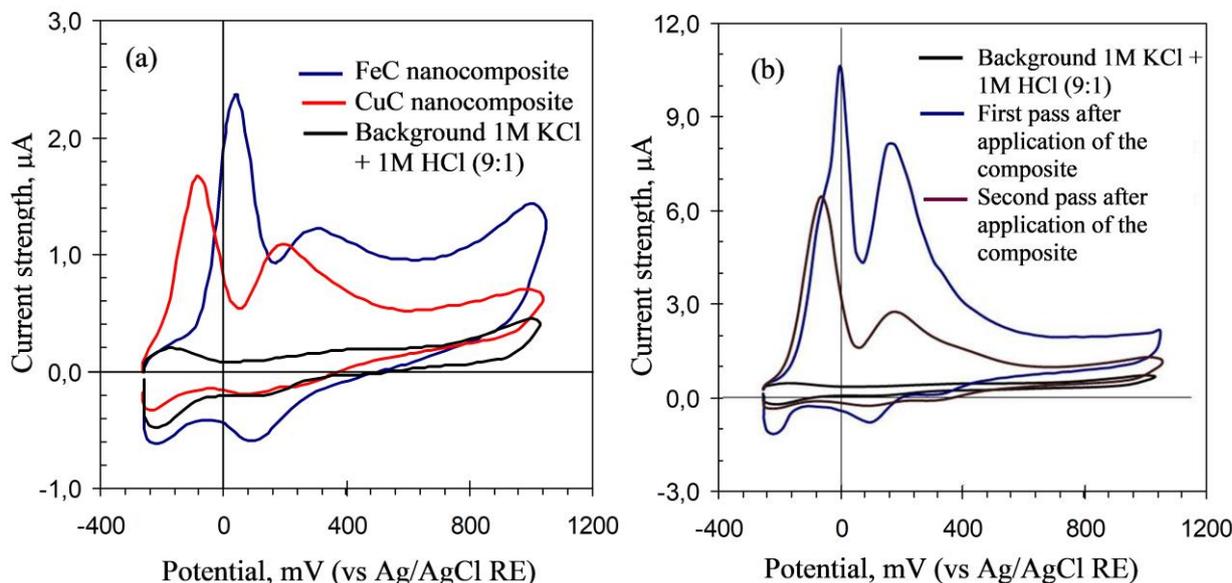
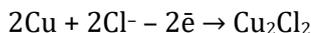
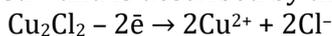


Fig. 3. Cyclic voltammograms of metal-carbon composites:
a - monometallic Fe and Cu-nanocomposites; b - FeCu-carbon nanocomposite

Analyzing the cyclic voltammogram of the monometallic copper-carbon nanocomposite, we can conclude that the first maximum is due to the oxidation of copper to the monovalent state. The +1 oxidation state for copper is unstable and easily disproportionates [25]. However, at a sufficiently high concentration of Cl⁻ ions in the solution, Cu⁺ is stabilized due to the formation of insoluble cuprum(I) chloride. The reaction that takes place at the electrode can be described by the equation:



The second peak in the voltammogram corresponds to the oxidation of cuprum(I) chloride to Cu²⁺ and is described by the equation:



It seems probable that the porous carbon carrier, which contains poorly soluble Cu₂Cl₂ salt, complicates the process of its electrochemical oxidation with increasing electrode potential.

The maxima on the cyclic voltammogram of the iron-carbon nanocomposite correspond to the following stages of iron oxidation:



Comparing the cyclic voltammograms for monometallic composites with the cyclic voltammogram for a bimetallic nanocomposite, we see that the curve for the bimetallic nanocomposite is a superposition of two curves for monometallics. The electrode was placed in the solution at a potential of -0.3 V relative to a saturated silver chloride electrode. At the same time, both copper and iron are in the form of simple substances (they are zerovalent). When the potential is scanned into the anode region, the current increases at potentials characteristic of the oxidation of both metals in a background solution. It can be concluded that iron was completely oxidized in two stages and Fe³⁺ ions diffused from the electrode surface into the solution. The second scan shows only peaks of copper, since in the chloride background this metal forms a poorly soluble cuprum(I) chloride (first peak), which in the anodic potential region gives Cu²⁺ ions, but they have less time to leave the electrode surface. Complete extraction of copper from the surface of the composite is possible after several scanning cycles.

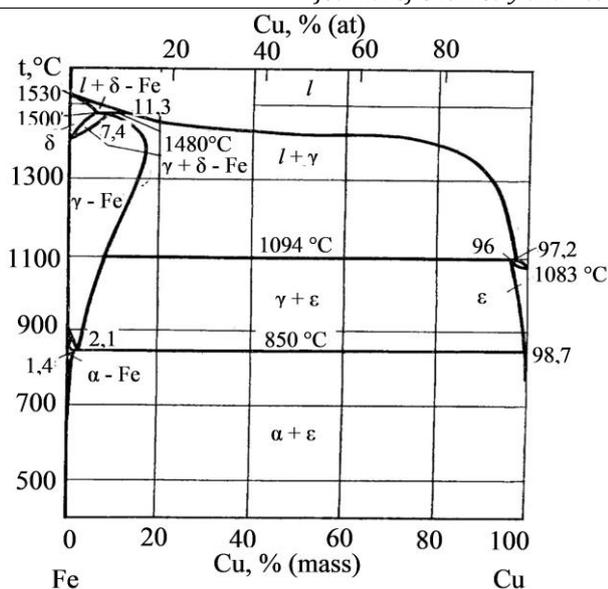


Fig.4. Diagram of the Fe-Cu system

In our opinion, this situation can be explained by the formation of fcc lattice common to both

metals, although the state diagram shows that these metals are practically insoluble in each other. However, in the 1990s, mechanical alloying (MA) was widely used to prepare homogeneous systems from components that do not mix in the molten state [23; 24]. As can be seen from the phase diagram of the Fe-Cu system (Fig. 4), the solubility of copper in iron is negligible (and vice versa). But MA-treatment made it possible to form this system at room temperature.

Electron microscopic images of FeCu@C nanocomposite revealed interesting features of nanocomposite morphology (Fig. 5). On the surface of the pieces of the amorphous matrix, since diffractometrically carbon nanoforms were not detected, there are numerous spherical formations. Their light color and the fact that they disappear after treatment with concentrated nitric acid indicates that they consist of metal.

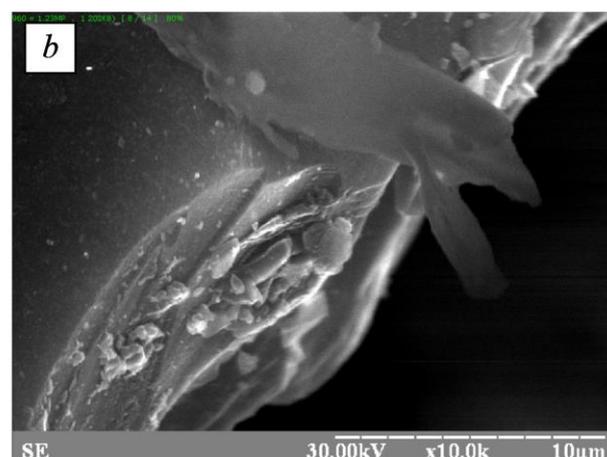
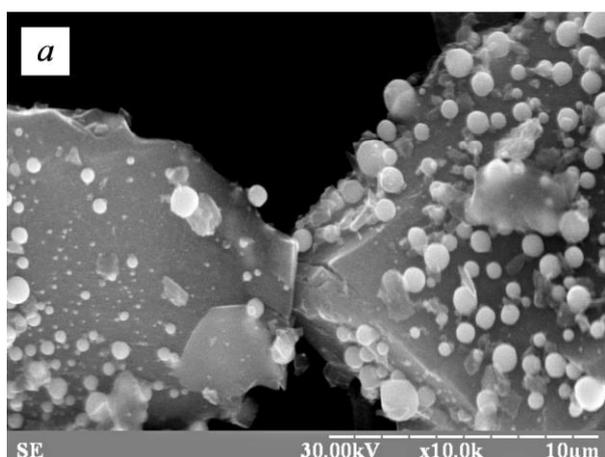


Fig. 5. SEM image of FeCu@C nanocomposite:
a - before treatment by concentrated HNO₃; b - after treatment by concentrated HNO₃

It is also interesting that on the fracture of some pieces of the composite it can be seen that these balls are present in the volume of the

composite and are placed in hexagonal cavities (Fig. 6).

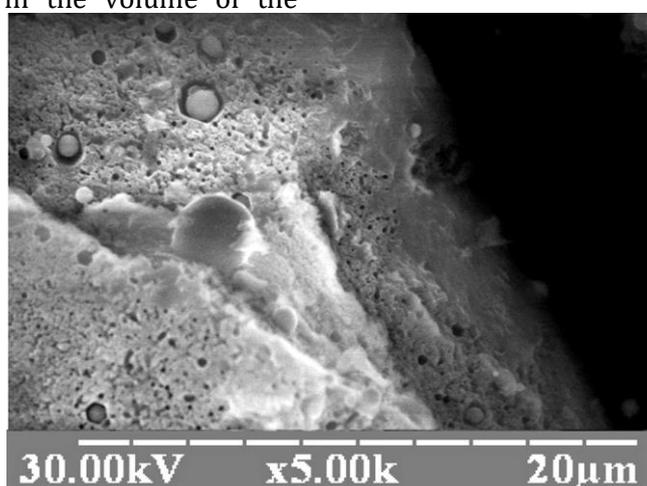


Fig. 6. SEM image of FeCu@C nanocomposite with hexagonal cavities

In addition, the standard acid treatment did not allow to completely remove both metals from the composite. This means the presence of dead pores in the carbon matrix. In Fig. 7 combines the spectra of the nanocomposite before and after the acid treatment, which show that the metal content has decreased by about half.

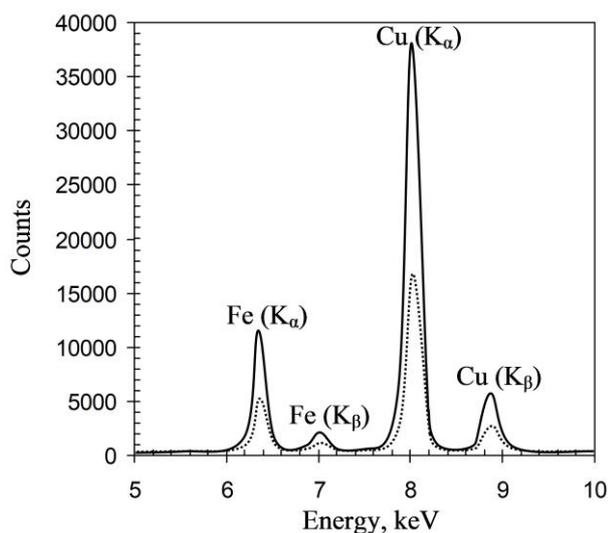


Fig. 7. Combined X-ray fluorescence spectra of FeCu@C nanocomposite before and after acid treatment

The obtained iron-copper nanocomposites were also investigated by SEM method combined with EDAX. Fig. 8 shows the distribution of Fe and Cu along the scan line and the distribution map of the elements (Fig. 9).

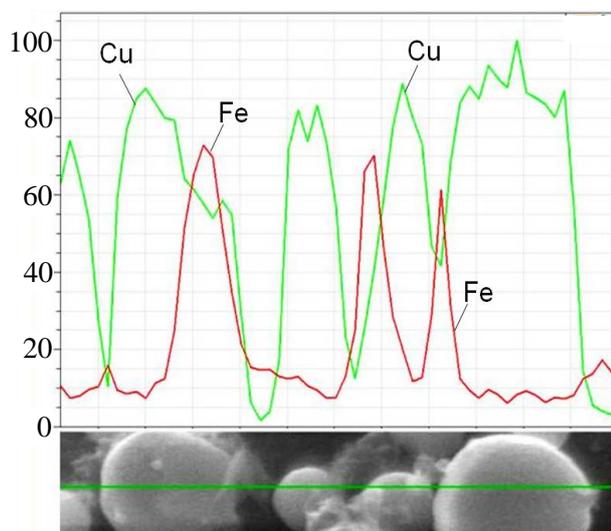


Fig. 8. Distribution of elements in FeCu@C nanocomposites along the scan line

From these data it follows that spherical formations consist mainly of copper, while iron is concentrated in the carbon matrix. The spherical shape of metal particles implies that the metal in the process of synthesis was in a molten, or close to it, state. This may be because the melting point

of 10 - 100 nm particles can be much lower than the melting point of a compact metal. But many spherical structures in SEM images are much larger.

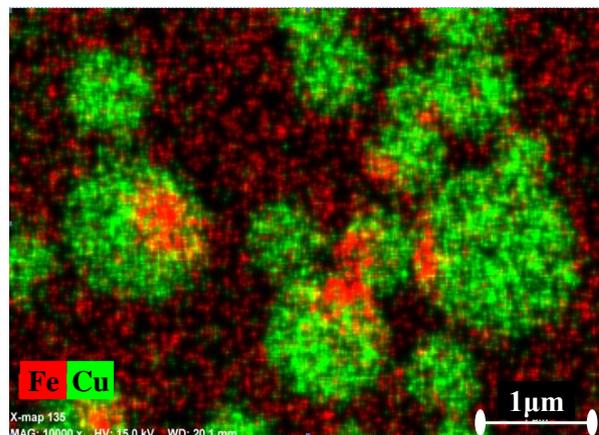


Fig. 9. Map of the distribution of elements in the composite

Testing for magnetic properties showed their absence in the FeCu@C composite, which may be due to either very small particle size or, more likely, the formation of a phase of the FeCu alloy with lattice parameters characteristic of copper.

Conclusion

The iron-copper nanocomposite was synthesized by pyrolysis of a mixture of iron (III) and copper (II) synthetic humates at a temperature of 800-900 °C in a reducing hydrogen atmosphere. Electron microscopy of the synthesized nanocomposite revealed morphological features in the form of metal spherical formations up to 700-1000 nm in size, located on the surface of the carbon matrix, which according to X-ray diffraction is amorphous. Energy-dispersion X-ray spectroscopy showed that spherical formations consist mainly of copper. No iron phase peaks were detected on the diffraction pattern. It was found that the iron-copper nanocomposite has good electrical conductivity, but no ferromagnetic properties, probably due to the fact that iron forms a common crystal lattice with copper fcc.

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References

- [1] Kang, J., Kim, Y., Kim, H., Hu, X., Saito, N., Choi, J., Lee, M. (2016). In-situ one-step synthesis of carbon-encapsulated naked magnetic metal nanoparticles conducted without additional reductants and agents. *Sci. Rep.*, 6, 1–10. <https://doi.org/10.1038/srep38652>

- [2] Muratov, D. G., Vasilev, A. A., Efimov, M. N., Karpacheva, G. P., Dzidziguri, E. L., Chernavskiy, P.A. (2019). Metal-Carbon Nanocomposites FeNi/C: Production, Phase Composition, Magnetic Properties. *Inorg. Mater. Appl. Res.*, 10, 666–672. <https://doi.org/10.1134/S2075113319030298>
- [3] Galaburda, M., Kovalska, E., Hogan, B. T., Baldycheva, A., Nikolenko, A., Dovbeshko, G. I., Oranska, O.I., Bogatyrov, V. M. (2019). Mechanochemical synthesis of carbon-stabilized Cu/C, Co/C and Ni/C nanocomposites with prolonged resistance to oxidation. *Sci. Rep.*, 9, 1–10. <https://doi.org/10.1038/s41598-019-54007-2>
- [4] Tan, H., Tang, G., Wang, Z., Li, Q., Gao, J., Wu S. (2016). Magnetic porous carbon nanocomposites derived from metal-organic frameworks as a sensing platform for DNA fluorescent detection. *Anal. Chim. Acta.*, 940, 136–142. <https://doi.org/10.1016/j.aca.2016.08.024>
- [5] Siddiqui, M.T.H., Baloch, H. A., Nizamuddin, S., Mubarak, N.M., Mazaric, S. A., Griffin, G.J., Srinivasan M. (2021). Dual-application of novel magnetic carbon nanocomposites as catalytic liquefaction for bio-oil synthesis and multi-heavy metal adsorption. *Renew. Energy.*, 172, 1103–1119. <https://doi.org/10.1016/j.renene.2021.02.157>
- [6] Alshammari, H. M., Alshammari, A. S., Humaidi, J. R., Alzahrani, S. A., Alhumaimess, M. S., Aldosari, O. F., Hassan, H. M. A. (2020) Au-Pd Bimetallic Nanocatalysts Incorporated into Carbon Nanotubes (CNTs) for Selective Oxidation of Alkenes and Alcohol. *Processes*, 8(11), 1380. <https://doi.org/10.3390/pr8111380>
- [7] Zarin, S., Aslam, Z., Zahir, A., Kamal, M. S., Rana, A. G., Ahmad, W., Ahmed S. (2018). Synthesis of bimetallic/carbon nanocomposite and its application for phenol removal. *J. Iran. Chem. Soc.*, 15, 2689–2701. <https://doi.org/10.1007/s13738-018-1457-1>
- [8] Efimov, M. N., Vasilev, A. A., Muratov, D. G., Zemtsov, L. M., Karpacheva G. P. (2017). Metal-carbon C/Co nanocomposites based on activated pyrolyzed polyacrylonitrile and cobalt particles. *Russ. J. Phys. Chem. A.*, 91, 1766–1770. <https://doi.org/10.1134/S0036024417090096>
- [9] Litvin, V.A., Abi Njoh, R. (2020). Synthetic fulvic acids from tannin. *J. Chem. and Technol.*, 28(3), 251–259. <https://doi.org/10.15421/082027>
- [10] Litvin, V.A., Abi Njoh, R. (2021) Quercetin as a precursor in the synthesis of analogues of fulvic acids and their antibacterial properties. *Vopr. khimii i khimicheskoi tekhnologii.*, 2, 56–64. <https://doi.org/10.32434/0321-4095-2021-135-2-56-64>
- [11] de Melo, B. A. G., Motta, F. L., Santana, M. H. A. (2016). Humic acids: Structural properties and multiple functionalities for novel technological developments. *Mater. Sci. Eng. C.*, 62, 967–974. <https://doi.org/10.1016/j.msec.2015.12.001>
- [12] Litvin V. A., Abi Njoh, R. (2020). Humic-like acid derived from 1,2-naphthoquinone. *Fr.-Ukr. J. Chem.*, 08(02), 140–149. <https://doi.org/10.17721/fujcV8I2P140-149>
- [13] Saiz-Jimenez C. (1994). Analytical Pyrolysis of Humic Substances: Pitfalls, Limitations, and Possible Solutions. *Environ. Sci. Technol.*, 28 (11), 1773–1780. <https://doi.org/10.1021/es00060a005>
- [14] [14] Swiatkowska-Warkocka Z. (2021). Bimetal CuFe Nanoparticles—Synthesis, Properties, and Applications. *Appl. Sci.* 2021, 11, 1978–1998. <https://doi.org/10.3390/app11051978>
- [15] Zhang, Y., Liao, Y., Shi, G., Wang, W., Su, B. (2020). Preparation, characterization, and catalytic performance of Pd-Ni/AC bimetallic nanocatalysts. *Green Process. Synth.*, 9, 760–769. <https://doi.org/10.1515/gps-2020-0071>
- [16] Ruan, Z., Ran, J., Liu, S., Chen, Y., Wang, X., Shi, J., Zhu, L., Zhao, S., Lin J. (2021). Controllable preparation of magnetic carbon nanocomposites by pyrolysis of organometallic precursors, similar molecular structure but very different morphology, composition and properties. *New J. Chem.*, 45, 2044–2052. <https://doi.org/10.1039/D0NJ05699E>
- [17] Manukyan, A., Elsukova, A., Mirzakhanyan, A., Gyulasyan, H., Kocharian, A., Sulyanov, S., Spasova, M., Römer, F., Farle, M., Sharoyan, E. (2018). Structure and size dependence of the magnetic properties of Ni@C nanocomposites. *J. Magn. Magn. Mater.*, 467, 150–159. <https://doi.org/10.1016/j.jmmm.2018.07.056>
- [18] Litvin, V. A., Galagan, R. L. (2017). Synthesis and properties of Co-carbon nanocomposites using synthetic fulvic acids. *Mater. Chem. Phys.*, 201, 207–213. <https://doi.org/10.1016/j.matchemphys.2017.08.055>
- [19] Litvin, V. A., Abi Njoh, R. (2021). Copper-carbon nanocomposites based on synthetic humic substances. *J. Chem. Technol.*, 29(1), 19–30. <https://doi.org/10.15421/082113>
- [20] Litvin, V. A., Galagan, R. L., Minaev, B. F. (2012). Synthesis and Properties of Synthetic Analogs of Natural Humic Acids. *Russ. J. Appl. Chem.*, 85(2), 296–302. <https://doi.org/10.1134/S1070427212020243>
- [21] Jenkins, R. and Smith, D. (1987). “Powder Diffraction File,” in Crystallographic Databases, edited by F. H. Allen, G. Bergerhoff, and R. Sievers, International Union of Crystallography, U.K., pp. 159–174.
- [22] Chatterjee S. K. (2008). Crystallography and the World of Symmetry. Springer, Berlin, Heidelberg XII. <https://doi.org/10.1007/978-3-540-69899-9>
- [23] Jiang, J. Z., Gente, C., Bormann R. (1998). Mechanical alloying in the Fe-Cu system. *Mater. Sci. Eng.*, 242, 268–277. <https://doi.org/10.4028/www.scientific.net/KEM.230-232.631>
- [24] Jeon, J. (2005). Synthesis, Microstructure, and Mechanical Behavior of Fe-Cu Composites. Master's Thesis. University of Tennessee, 136.
- [25] Brainina, H.Z., Neiman E. Ya. (1982). Solid-phase reactions in electroanalytical chemistry, Moscow: Chemistry. (in Russian)