doi: 10.56761/EFRE2024.S4-P-022301

Radiation-chemical synthesis of ferrihydrite - SiO_2 composite

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Abstract. The radiation-chemical method is used to synthesize composite mesoporous nanoparticles (NPles) "ferrihydrite (Fhy) – silicon dioxide" in isopropyl alcohol. The inhibitory effect of the additive of commercial NPles SiO_2 (Aerosil 90) on the solubility of Fhy in water was found; a tenfold increase in the main texture parameters of the Fhy-SiO_2 composite (specific surface area (SSA) and pore volume) compared to pure Fhy). Electron diffraction analysis (EDX) and mapping confirmed the uniform distribution of NPles Fhy over the surface of SiO_2 particles.
Keywords: ferrihydrite, Fhy-SiO_2 composite, radiation-chemical synthesis.

1. Introduction

Ferrihydrite (Fhy) is a natural, nanoscale, amorphous mineral of iron oxyhydroxide present in most biological and geochemical media [1]. The role of Fhy is significant as a precursor for the synthesis of nanoparticles (NPles) hematite, as well as due to the unique properties of Fhy itself, interest in methods for the synthesis of ferrihydrite is steadily growing.

Ferrihydrite is a biocompatible material, characterized by high reactivity and high adsorption capacity of ions, paramagnetic at room temperature, with variable band gap from 1.3–2.5 eV [1, 2]. Such properties make it possible to use Fhy in many fields of science and technology, for example, in the metallurgical industry, for wastewater treatment, in lithium-ion batteries, in magnetic applications, in agriculture, in biomedicine and oncology [2, 3]. Most Fhy synthesis methods are based on chemical precipitation routes, however these methods require multi-stage purification and long time to produce the final product, so the ability to produce large amounts of Fhy NPles is still a challenge. Silicon dioxide is a widespread oxide in nature, so research is very widely conducted on the interaction between Fhy and SiO_2 [4].

The purpose of this work is to produce a Fhy-SiO_2 nanocomposite using a one-step, environmentally friendly, scalable radiation-chemical method [5–7] and to study its individual physicochemical characteristics to assess their potential use in biomedicine. The innovative Fhy synthesis procedure is central to this work. The properties of composite NP Fhy-SiO_2 were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurement (SSA) by Brunauer-Emmett-Teller (BET) and X-ray photoemission spectroscopy (XPS).

2. Experimental

2.1. Synthesis method

The synthesis of the nanocomposite Fhy-SiO_2 was carried out using the radiation-chemical method [1–4]. Deposition of Fhy nanoparticles was carried out continuously, during their synthesis using a pulsed electron beam (electron energy 500 keV), in a liquid medium-alcohol suspension with commercial SiO_2 nanoparticles (Aerosil 90, Degussa).

2.2. Samples characterization

X-ray diffraction (XRD) analysis was conducted using a D8 DISCOVER diffractometer (Cu $K\alpha_{1,2}$ $\lambda = 1.542$ Å) with a graphite monochromator on a diffracted beam, employing the TOPAS 3 program. Texture analysis was performed using a Micromerics TriStar 3000 V6.03 Analyzer (a preliminary degassing of the sample for 1 hour at a temperature of 100 ºC). The scanning electron microscopy (SEM) morphology studies and chemical analyses were taken with an analytical scanning electron microscope Zeiss Merlin working at 10–20 kV and equipped with an

energy dispersive X-ray detector Oxford Instruments INCA x-act. Photoemission (PE) spectra were measured using a hemispherical analyzer within an ESCALAB 250 Xi laboratory spectrometer (Thermo Fisher Scientific, UK).

3. Results and discussion

3.1. X-ray diffraction analysis

The Fig. 1a shows an X-ray diffractogram of the composite powder Fhy-SiO_2. Diffractorms of NP pure Fhy and NP Aerosil 90 are given in the works [7, 8]. XRD pattern of 2L Fhy were two wide diffusion peaks ($2\theta = 33.5°$ and $60.7°$) correlated to the (110) and (115) planes of 2-lines ferrihydrite [9]. The average crystallite size of NPles, calculated using a modified Scherrer formula, was determined to be ~ 0.8–1 nm. The maximum position on the diffractogram of the composite corresponds to an angle of $2\theta = 21.3°$, an approximate particle size of 0.6 nm. The position of this diffraction peak corresponds to the maximum at NP Aerosil 90 [8]. A closer look shows that diffraction peaks at $2\theta = 33.5°$ and $60.7°$ from Fhy are also present on the diffractory of the composite. The superposition of the diffraction peaks Fhy and SiO_2 indicates that there is no chemical interaction between the two phases when Fhy nanoparticles synthesized from iron (III) nitrate are precipitated onto the surface of NPles SiO_2 pre-dispersed in an isopropyl alcohol liquid medium. The appearance of the composite (Fig. 1b) indicates an uneven distribution of Fhy particles over the surface of the NPles SiO_2.

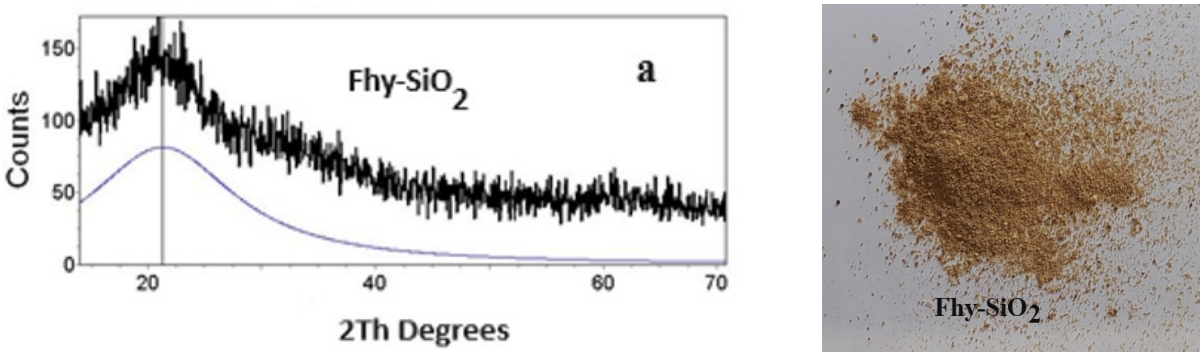

Fig. 1. (a) –XRD pattern of composite Fhy-SiO_2, (b) – Appearance of NP composite NP Fhy-SiO_2.

3.2. Barrett-Joyner-Halenda (BJH) Analysis

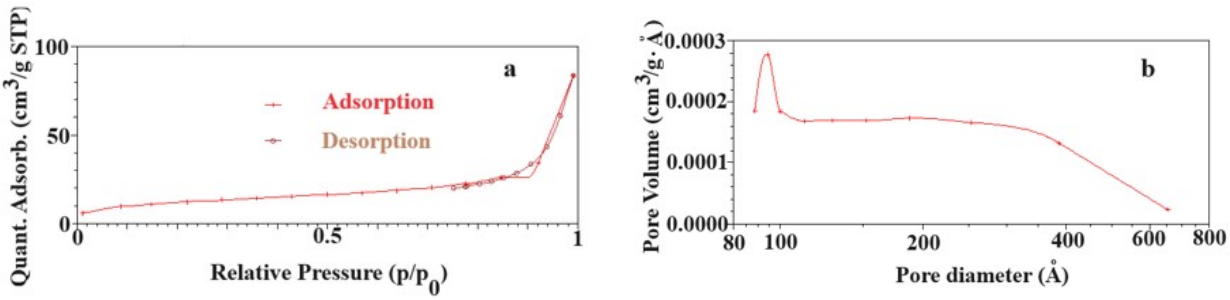

Fig. 2. (a) – Isotherm of adsorption and desorption for sample composite Fhy-SiO_2, (b) – Pore size distribution for sample composite Fhy-SiO_2.

The Fig. 2 shows the isotherms of the nitrogen disorption assembly and the pore size distribution for the Fhy-SiO_2 composite. The absence of a well-defined hysteresis loop, a characteristic feature of mesoporous materials, could have been caused by the high density of the sediment layer formed by Fhy NPles on the surface of SiO_2 nanoparticles in alcohol suspension. A similar hysteresis loop is observed on the nitrogen adsorption-desorption isotherm of the Fhy-SiO_2

nanocomposite. A comparison of the texture characteristics of pure Fhy and composite Fhy-SiO_2 given in Table 1 showed that the texture properties of the composite were superior to those of pure Fhy. The specific surface area (SSA) of the composite was 14 times the SSA of Fhy, respectively, the pore volume of the composite was 5.5 times the pore volume of Fhy, with an equal pore diameter (about 30 nm) in both powders. Both materials had similar bimodal pore size distribution, with maxima at 7–9 and 20–25 nm.

Table 1. Texture characteristics of NP pure Fhy and composite Fhy-SiO_2.

Sample	SSA, m2/g	Vpore, cm3/g	Dpore, nm
Fhy	2.97 [4]	0.020	29.9
Fhy-SiO2	41.91	0.111	29.3

3.3. Scanning Electron Microscopy

EDX analysis (Fig. 3a) showed the presence of basic elements-O, Fe and Si in the composite and the absence of any related impurities. In the SEM image (Fig. 3b) of the composite Fhy-SiO_2, it is clearly seen that the composite is fragments of porous coating, of arbitrary shape and size, with a rough surface, which is consistent with the texture analysis data. Element mappings (Fig. 3c, 3d, 3e) of Fhy-SiO_2 composite provide direct evidence that Fe ions are uniformly dispersed among the amorph SiO_2 nanoparticles.

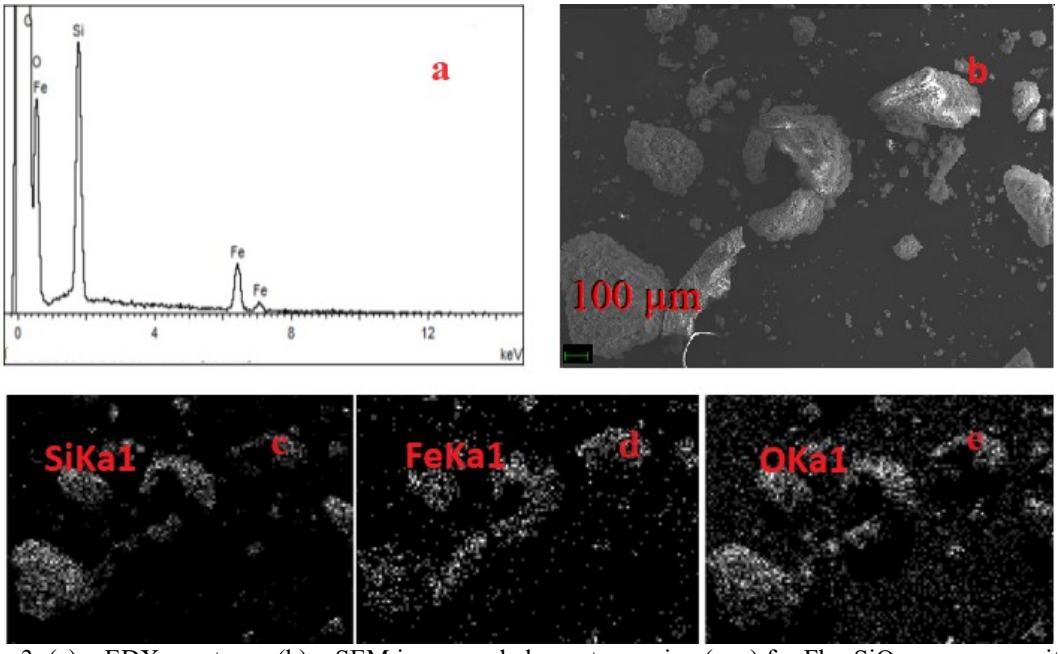

Fig. 3. (a) – EDX spectrum, (b) – SEM image and element mapping (c–e) for Fhy-SiO_2 nanocomposite.

The Table 2 shows the results of the elemental EDX analysis of the Fhy-SiO_2 composite sample from three different sections of the sample. The average concentration of elements in the composite (at. %) is O-80.91, Si-14.43 and Fe-4.66.

Table 2. The concentration of elements (in at%) in three areas of the composite Fhy-SiO_2.

	[O]	[Si]	[Fe]
1	84.87	10.90	4.24
2	78.20	16.48	5.33
3	79.67	15.91	4.42

3.4. X-ray photoemission spectroscopy

The results of elemental analysis of the surface of the nanoparticles of the composite Fhy-SiO_2 and pure Fhy performed by X-ray photoemission spectroscopy (XPS) are given in the Table.3. The O/Si ratio in the composite (2.08) is very close to stoichiometric, which confirms that the main component of the composite is silica, and the low Fe concentration (0.93 at.%) indicates neither the insignificant concentration of NPles Fhy on the surface of the NPles SiO_2 and their most likely placement inside the interparticle pores in the depth of the composite. Note that the concentration of impurity carbon and nitrogen atoms on the surface of the composite is almost 14 and 11 times higher than the concentration of carbon and nitrogen in pure Fhy. The low concentration of N and C impurity atoms in the composite indicates inhibition of the surface chemical activity of pure Fhy nanoparticles after their adsorption on the surface of SiO_2 nanoparticles. The inhibitory effect of SiO_2 also influenced the solubility of pure Fhy in water [7]; solubility decreased dramatically, which led to the formation of an aqueous suspension of composite NPles.

Table 3. Chemical composition of the samples Fhy and Fhy-SiO_2 by XPS.

Sample	Concentration, at. %						
	[O]	[Si]	[Fe]	[N]	[C]	O/Fe	[O/Si]
Fhy-SiO_2	63.90	30.74	0.93	0.4	4.03	68.71	2.08
Fhy [7]	40.5	–	11.1	5.5	42.9	3.6	–

4. Conclusion

For the first time, using the radiation-chemical method, synthesis of composite mesoporous nanoparticles "ferrihydrite-silicon dioxide" was carried out in a liquid alcohol suspension of commercial NPles SiO_2. A one-step and short-term method for the synthesis of such composite NPles, promising for their use in biomedicine, can be easily scaled on an industrial scale.

Acknowledgement

The authors are grateful to the junior research scientist IEP UB RAS Demina T.M. for measurement of texture properties of NPs and the junior research scientist IEP UB RAS Demidova K.I. for XRD analysis. The reported study was funded by Russian Science Foundation, project number 22-19-00239.

5. References

[1] M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, Weinheim:Wiley-VCH, 2003.

[2] L. Macera, G. Taglieri, V. Daniele, M. Passacantando, F. D'Orazio, Nano-Sized Fe(III) Oxide Particles Starting from an Innovative and Eco-Friendly Synthesis Method, *Nanomaterials*, vol. **10**(323), 1, 2020; doi:10.3390/nano10020323

[3] Y. Wang, L. Deng, A. Caballero-Guzman, B. Nowack, Are engineered nano iron oxide particles safe? An environmental risk assessment by probabilistic exposure, effects and risk modelling. *Nanotoxicology*, vol. **10**, 1545, 2016; doi.org/10.1080/17435390.2016.1242798

[4] Y. Song, Z. Zhao, J. Li, Y. You, X. Ma, J. Li, X. Cheng, Preparation of silicon-doped ferrihydrite for adsorption of lead and cadmium: Property and mechanism, *Chin. Chem. Lett*., vol. **32**, 3169, 2021; doi.org/10.1016/j.cclet.2021.03.001

[5] M.E. Balezin, S.Yu. Sokovnin, and M.A. Uimin, *J. Phys.: Conf. Ser.*, vol. **2064**, 012086, 2021; doi: 10.1088/1742-6596/2064/1/012086

[6] M.E. Balezin, V.V. Bazarnyi, E.A. Karbovnichaya, S.Yu. Sokovnin, Application of Nanosecond Electron Beam for Production of Silver Nanopowders, *Nanotech. in Russia*, vol. **6**(11–12), 757, 2011; doi: 10.1134/S1995078011060036
[7] V.G. Ilves, M.E. Balezin, S.Yu. Sokovnin, A.S. Gerasimov, E.G. Kalinina, D.S. Rusakova, P.M. Korusenko, M.G. Zuev, M.A. Uimin, *Rad.Phys.Chem*, vol. **218**, 111612, 2024; doi: 10.1016/j.radphyschem.2024.111612
[8] V.G. Ilves, S.Yu. Sokovnin, S.A. Uporov, M.G. Zuev, *Phys. Solid State*, vol. **55**, 1262, 2013; doi: 10.1134/S1063783413060127
[9] Z. Li, T. Zhang, K. Li, One-step synthesis of mesoporous two-line ferrihydrite for effective elimination of arsenic contaminants from natural water, *Dalton Trans*, vol. **40**, 2062, 2011; doi: 10.1039/c0dt01138j