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Radiation-chemicalsyntesis of composite ferrihydrite-silver

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Abstract. Radiation-chemical method is applied for synthesis of mesoporous composite of nanoparticles "ferrihydrite (Fhy) -silver" in isopropyl alcohol. Iron and silver nitrates were used as precursors. Elemental analysis by EDX and XPS showed the presence of O, Fe and Ag in the final product. The SSA of the composite (1.70 m^2/g) decreased relative to the SSA of pure Fhy (2.97 m^2/g). XRD showed the presence of metallic NPles Ag (21.4 wt.%) in the composite and a significant amount of precursor crystals $AgNO_3$. The presence of metal NPles Ag and semiconductor Fhy makes it possible to count on the appearance of plasmon resonance in such heterophasic structures. Ag nanoparticles suppress the solubility of the composite in water, and the presence of iron in the composite leads to the appearance of a magnetic moment in it.
Keywords: ferrihydrite, Fhy-Ag nanocomposite, radiation-chemical synthesis.

1. Introduction

Ferrihydrite (Fhy) is a typical iron nanoxide (oxyhydride), with a large specific surface area (SSA > 200 m^2/g), a nanoscale structure, an abundance of Fe-OH surface groups, so Fhy is very attractive as a Fenton catalyst [1]. Fhy shows a higher level of Fenton oxidation of 2,4,6-trinitrotoluene than other iron minerals (e.g., hematite, goethite, etc.). The Fhy nanostructured properties in the Fenton system provide good contact between Fhy, H_2O_2 and contaminants and promote uniform dispersion of materials.

A new heterogeneous photophenton catalyst, Ag/AgBr/Fhy (Ag/AgBr/Fhy), has recently been developed by combining AgBrwithFhy and then generating Ag nanoparticles in-situ on the AgBr/Fhy surface [2]. The radiation chemical method (RCM) has previously been used to produce Ag nanoparticles in various media [3]. Taking into account the known antibacterial properties of silver and the successful use of magnetoferritin nanoparticles for targeting and visualizing tumour tissues [4] (ferritin nucleus contains NPles ferrihydrite), it was of particular interest to use RCM for the synthesis of Ag-Fh nanocomposite from an alcohol solution of Ag and Fe nitrates and to study the main physical chemical characteristics and possibilities of using the nanocomposite in biomedicine.

The purpose of this work is to produce the Fhy-Ag nanocomposite using the radiation-chemical method [3, 5–7] from an isopropyl solution of two nitrate iron and silver, and to study the separate physicochemical characteristics of the composite to assess its potential use in biomedicine and photocatalysis. The innovative procedure for the simultaneous synthesis of the metal-oxide composite is central to this work.

2. Experimental

2.1. Synthesis method

The synthesis of the Fhy-Ag nanocomposite was carried out using the radiation-chemical method [3, 5–7]. The synthesis of Fhy and Ag nanoparticles was carried out continuously using a pulsed electron beam (electron energy 500 keV), in a liquid medium-isopropyl solution of $AgNO_3$ nitrates and Fe $(NO_3)_3$ in a mass ratio of 1:1.

2. 2. Samples characterization

X-ray diffraction (XRD) analysis was conducted using a D8 DISCOVER diffractometer (Cu Kα1,2 λ = 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. XRD analysis

The Fig.1 shows an X-ray diffractogram of Fhy-Ag composite powder.The composite contained two crystalline phases: silver nanocrystals (cubic phase, S.G.: Fm-3m (225), ≈ content 21 wt.%, coherent scattering region (CSR) = 38 ± 3 nm, period a = 4.088 ± 0.002 Å, R_{bragg} = 3.831) and nanocrystals of one of the precursor $AgNO_3$ (orthorhombic phase, S.G.: Pbca (61), contents ≈ 79 wt. %, CSR = 90 ± 5 nm, a periods = 6.995 ± 0.003) Å, b = 7.332 ± 0.003 Å, c = 10.119 ± 0.005 Å, R_{bragg} = 8.746, R_{exp} = 13.71, R_{wp} = 37.34). The formation of Fhy nanoparticles by the XRD method is not confirmed, possibly due to the extremely small size of ferrihydrite nanoparticles (less than 2nm), or the insignificant concentration of Fhy in the final synthesis product. The appearance of the composite powder (Fig.1b) confirms its crystalline nature-nanoparticles shine in the light, gray color confirms the presence of Ag in the powder. Simple experiments have shown (Fig.1c) that the NPles of the Fhy-Ag composite does not dissolve in water, unlike the NPles of pure Fhy, which dissolve in water almost instantly [7], while the NPles of the Fhy-Ag composite is attracted by a permanent magnet, which proves the presence of magnetic moment in the particles of the composite and confirms the presence of iron in it. The particles of the composite were perfectly held on the surface of water and did not dissolve in it for several days at room temperature, which indicates a reliable inhibition by Ag nanoparticles of the surface of $AgNO_3$ and Fhy nanocrystals, which are easily soluble in water.

Fig. 1 (a) XRD pattern of composite Fhy-Ag_2;(b) Fhy-Ag composite nanopowder; (c)Fhy-Ag composite nanoparticles on the surface of H_2O.

3.2. BJH analysis

The Fig. 2 shows the isotherms of the nitrogenadsorption-desorption and the pore size distribution for the Fhy-Ag composite. The presence of a hysteresis loop on the adsorption-desorption isotherm on the Fig. 2a indicates a mesoporous type of composite powder. Comparison of the texture characteristics of pure Fhy [7] and the Fhy-Ag composite given in Table 1 showed that the texture properties of the composite deteriorate compared to the texture properties of pure Fhy (the specific surface area (SSA) of the composite decreased by almost 2 times, the pore volume decreased by 10 times, the pore diameter decreased by almost 3 times). However, the multimodal pore size distribution in the Fhy-Ag (Fig. 2b) composite showed that most of the pores did not exceed 10 nm. Essentially, the addition of Ag nanoparticles to the FhyNPles, led to the filling of large diameter pores (29.9 nm) in pure Fhy, an increase in the proportion of oxygen atoms in the

mesoporous composite compared to pure Fhy, and the appearance of the "buoyancy" effect of the NPles composite in H_2O (Fig. 1c).

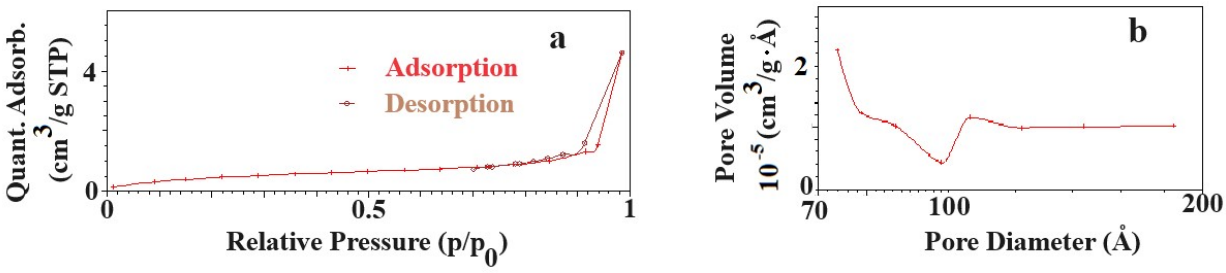

Fig. 2. (a) Isotherm of adsorption-desorption for sample composite Fhy-Ag; (b) Pore size distribution for sample composite Fhy-Ag.

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

Sample	*SSA*, m^2/g	V_{pore}, cm^3/g	D_{pore}, *nm*
Fhy	2.97 [7]	0.020	29.9
Fhy-Ag	1.70	0.002	12.9

3.3. SEM

EDX analysis (Fig. 3a) showed the presence of basic elements-O, Fe and Ag 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. Element mappings (Fig. 3c, 3d, 3e) of Fhy-Ag composite provide direct evidence that all elements (O, Fe and Ag) are uniformly distributed in the sample.

The Table. 2 shows the results of elemental EDX analysis of the Fhy-Ag composite sample from three different sections of the sample. The average concentration of elements in the composite (at.%) is O-80.55, Fe-3.88 and Ag-15.61.

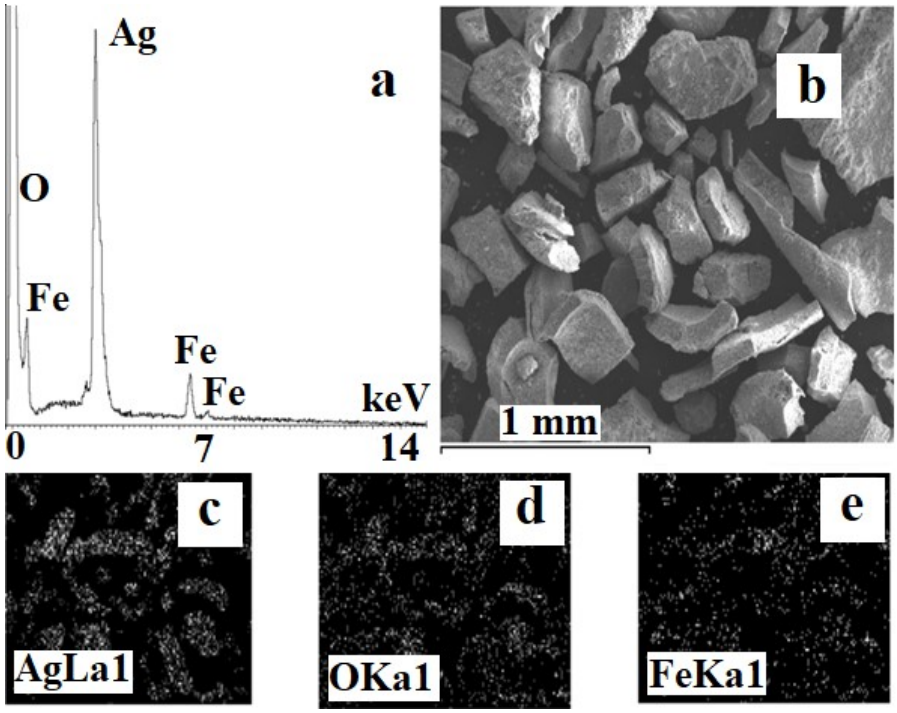

Fig. 3. EDX spectrum (a), SEM image (b) and element mapping for Fhy-Agnanocomposite (c-e).

Table 2. Concentration of elements (in at%) in three areas of the composite Fhy-Ag.

	[O]	[Fe]	[Ag]
1	80.97	4.15	14.88
2	79.85	4.11	16.04
3	80.84	3.25	15.91

3.4. XPS

The results of elemental analysis of the surface of the nanoparticles of the Fhy-Ag composite and pure Fhy performed by X-ray photoemission spectroscopy (XPS) are given in the Table.3. The concentrations of Ag in the composite determined by the EDX and XPS methods were substantially the same (15.61 and 13.36 at.%), respectively. The oxygen content of the composite is 1.6 times higher than that of pure Fhy, which supports the assumption of a high oxygen content of the composite made above. Curiously, XPS analysis showed the absence of nitrogen atoms in the composite, while their XRD data suggests that nitrogen atoms should be present in the sample, since it contains crystals of $AgNO_3$ in a significant amount, ≈ 79 wt.%. Assuming that all iron atoms go to the formation of Fhy in both samples from Table 3, from the comparison of the ratios of [O/Fe] atoms of the samples, it becomes clear that the mesoporous Fhy-Ag composite "captures" a significantly larger number of oxygen atoms than pure Fhy, which manifests itself in the synergistic effect of the joint presence of oxygen and silver atoms, manifested in the absence of solubility composite in water.

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

Sample	Concentration, at. %					
	[O]	[Fe]	[N]	[C]	[Ag]	[O/Fe]
Fhy-Ag	63.90	7.77	-	27.60	13.36	8.2
Fhy [7]	40.5	11.1	5.5	42.9	-	3.6

4. Conclusion

For the first time, using the radiation-chemical method, in an alcoholic solution of two iron and silver nitrates, the synthesis of the mesoporous nanocomposite "ferrihydrite-silver" was carried out. Structural, textural and morphological characteristics of the composite have been studied, which suggest that the synthesized composite is promising for use as a contrast agent in magnetic resonance imaging and for drug delivery.

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