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Synthesis and properties of ternary composite ferrihydrite-SiO_2-silver

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Abstract. The radiation-chemical method is used to synthesize a mesoporous composite of nanoparticles "ferrihydrite-SiO_2-silver" in isopropyl alcohol. Iron and silver nitrates were used as precursors. Elemental analysis by EDX and XPS showed the presence of O, Fe, Si and Ag in the final product. The specific surface area of the composite (29.81 m^2/g) increased relative to the area of pure ferrihydrite (2.97 m^2/g). XRD showed the presence of metallic nanoparticles Ag (21.36 wt.%) in the composite and a significant amount of precursor crystals $AgNO_3$. The presence of metal nanoparticles Ag and semiconductor ferrihydrite 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

Mesoporous ferrihydrite -SiO_2 composites can be used as adsorbents to remove formaldehyde from the air [1]. Studies of co precipitation of various iron oxides, in particular ferrihydrite (Fhy), with silicon oxide attract constant attention of environmental researchers [2]. When using the radiation-chemical method [3, 4], the coprecipitation of Ag and Fhy nanoparticles (NPles) formed in the alcohol suspension of SiO_{2NPles} (were used commercial $SiO_{2nanopowder}$ Aerosil90 (Degussa) with silver and iron nitrates is quite simply realized during the electron irradiation process. The purpose of the present work is to explain the processes of coprecipitation of the nanoparticles of the ternary composite Fhy-SiO_2-Ag and to study its characteristics.

2. Experimental

2.1. Synthesis method

The synthesis of the nanocomposite was Fhy-SiO_2-Ag carried out using a radiation-chemical method. Synthesis of Fhy and Ag NPles was carried out continuously using a pulsed electron beam (electron energy ~500 keV), in a liquid medium mixture of an alcohol (100 ml) suspension of NPles Aerosil90 (0.22 g) with $AgNO_3$ and $Fe(NO_3)_3$ dissolved in nitrates in a mass ratio of 1:1 (0.6 g). During the synthesis, NPles Ag and Fhy ($Fe_5HO_8 \cdot 4H_2O$) were simultaneously formed, which were simultaneously precipitated on amorphous NPles SiO_2 dispersed in isopropyl alcohol.

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 the composite powder Fhy-SiO_2-Ag. According to XRD analysis, the composite contained one crystalline phase: – $AgNO_3$ (orthorhombic phase, S.G.: Pbca (61), CSR >> 200 nm, periods a = 7.006±0.002 Å, b = 7.338±0.002 Å, c = 10.122±0004 Å, R_{bragg} = 12.111, R_{exp} = 10.73, R_{wp} = 14.18). A characteristic halo at low angles on the diffractoram indicates the possible presence of an amorphous component in the composite. However, the formation of NPles of two banded ferrihydrite (2L Fhy) and metallic crystalline NPles Ag by XRD has not been confirmed, possibly due to the extremely small size of the ferrihydrite NPles (less than 2nm) and the negligible concentration of crystalline NPles Ag in the final synthesis product. The coffee-white uneven color of the ternary composite (Fig. 1b) confirms that in the composite, Fhy nanoparticles (NPles of pure Fhy have a dark coffee color [7]) are still present. Unlike NPlesFhy-Ag, the nanoparticles of the ternary composite do not form a stable suspension in distilled water and immediately settle on the bottom of the Petri dish (Fig.1c), moreover, they do not dissolve in water, unlike NPles pure Fhy [7] and do not move in water when a permanent magnetic field is applied.

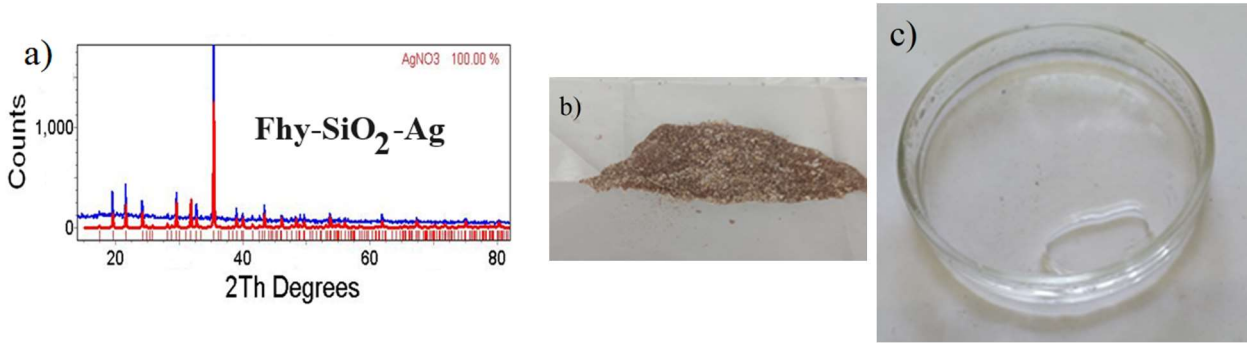

Fig. 1. Fhy-SiO_2-Ag composite: a) XRD pattern; b) photo; c) suspension in H_2O.

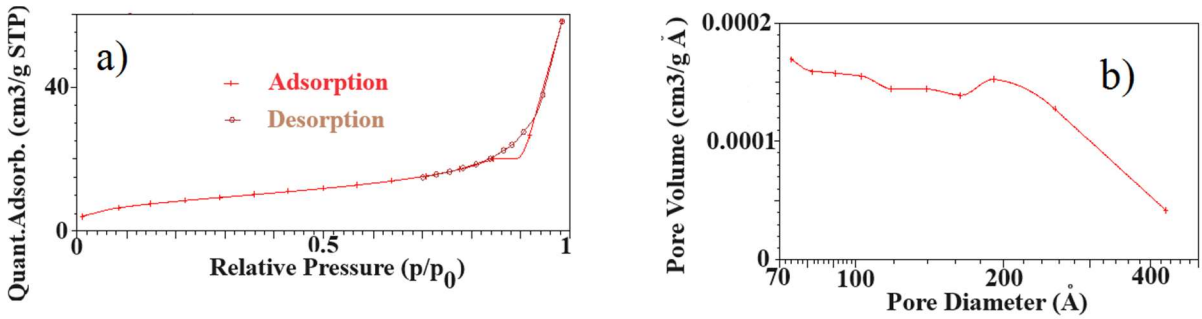

Fig. 2. Fhy-SiO_2-Ag composite: a) Isotherm of adsorption and desorption; b) Pore size distribution.

3.2. BJH analysis

The Fig. 2 shows the nitrogen adsorption-desorption isotherms and the pore size distribution for the Fhy-SiO_2-Ag composite. The hysteresis loop on the adsorption desorption isotherm on the Fig.2a indicates the presence of mesopores in the composite. Comparison of texture characteristics of pure Fhy [7] and dual Fhy-Ag composite with texture properties of ternaryFhy- SiO_2-Ag composite (Table 1) showed that texture parameters of ternary Fhy-SiO_2-Ag composite significantly exceeded corresponding characteristics of Fhy and Fhy-Ag (specific surface area (SSA) of composite by 10–18 times, pore volume (V_{pore}) by 4–40 times), However, the texture parameters of the ternary composite were inferior to those of the double composite with Fhy-SiO_2. The wide distribution of pores by size in the ternary composite (from 7 to 44 nm) did not have pronounced maxima, unlike the rest of the composite images in Table 1. Analysis of the change in SSA

composites showed that the introduction of Ag into nanocomposites greatly reduces the SSA of precursors (Fhy and NP Aerosil90 (SSA = 90 m^2/g), and the deposition of Ag and Fhy on the NPles Aerosil90 in isopropanol increases the pore volume of the composites.

Table 1. Texture characteristics of the pure NP Fhy, binary compositesFhy-Ag, Fhy-$SiO_2$and ternary composite Fhy-SiO_2-Ag.

Sample	SSA, m^2/g	V_{pore}, cm^3/g	D_{pore}, nm
Fhy	2.97 [7]	0.020	29.9
Fhy-Ag	1.7	0.002	12.9
Fhy-SiO_2	41	0.111	29.3
Fhy-SiO_2-Ag	29.81	0.080	23.4

3.3.SEM analysis

On Fig. 3 shows a morphological surface pattern of a ternary Fhy-SiO_2-Ag nanocomposite using SEM images taken at different magnifications. The finished product of the synthesis was large fragments of a coating of various sizes with an arbitrary shape. The main volume of such fragments was occupied by agglomerates of NPles SiO_2 (Fig. 3a) up to several tens of μm in size. Individual agglomerates of arbitrary shape (in Fig. 3b such a spherical-shaped agglomerate coated with quasi-spherical NPles Ag is exemplified) containing non-agglomerated NPles Ag were in disorder distributed over the surface and in the depths of larger agglomerates based on NPles SiO_2. Mesopores on the surface of the composite, less than 50 nm in size, are clearly visible on the Fig. 3, which confirms the results of the textural analysis of the ternary composite.

EDX analysis (Fig. 4a) showed the presence of basic elements-O, Si, Fe and Ag in the composite and the absence of undesirable impurities. In SEM image and element mappings (Fig. 4b-f) of Fhy-SiO_2-Ag composite provide direct evidence that all elements (O, Si, Fe and Ag) are not uniformly distributed over the sample. The Table.2 shows the results of elemental EDX analysis of the Fhy-SiO_2-Ag composite sample from three different sections of the sample. Average concentrations of elements in the composite (in at.%): O-79.02, Si-10.91, Fe-8.58 and Ag-1.48.

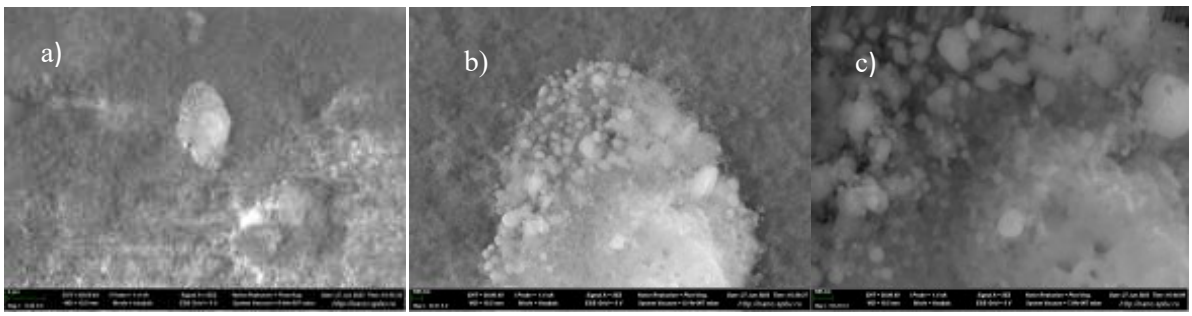

Fig. 3. SEM image of composite Fhy-SiO2-Ag with different magnification (a) an ellipsoid-shaped composite particle of about 4-5 μm on the surface of Aerosilnanoparticles; (b) surface of a spheroidal NPlescomposite coated with NPles Ag of a quasi-spherical shape of 20 to 100 nm (c) a scattering of quasi-spherical NPles Ag on a mesopores supported surface of agglomerated NPlesAerosil

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

Sample	[O]	[Si]	[Fe]	[Ag]
1	80.96	14.02	3.04	1.98
2	80.38	15.07	2.951	1.6
3	75.72	3.68	19.75	0.85

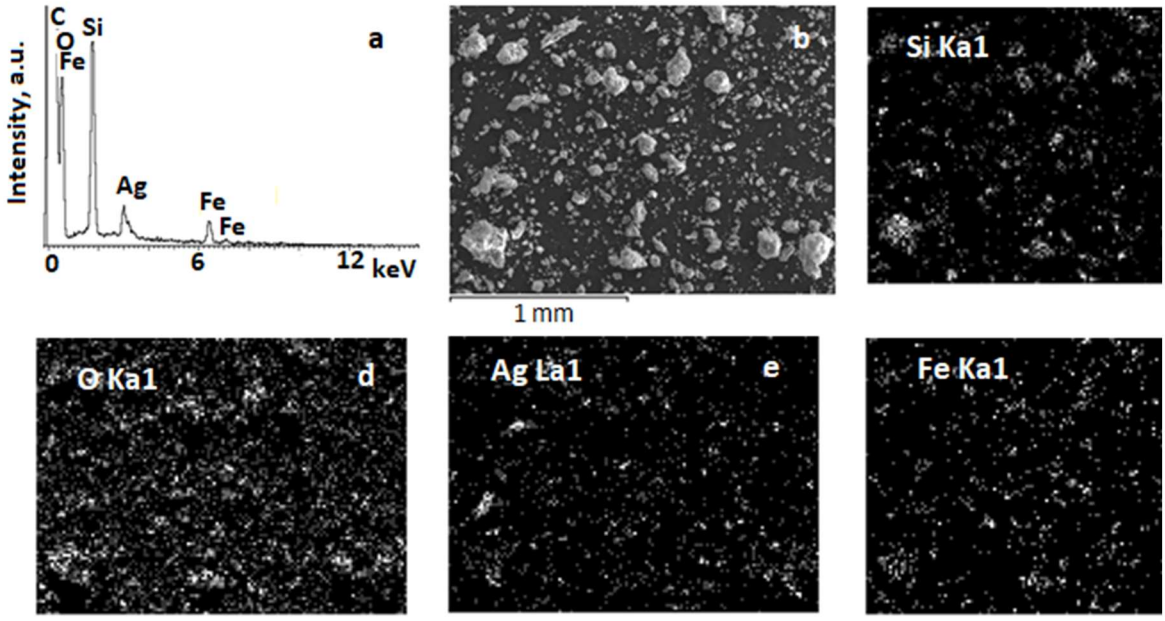

Fig. 4. Results of the EDX analysis.

3.4. XPS analysis

The results of elemental analysis of the surface of the NPlesof the composite Fhy-SiO_2- Ag and pure Fhy performed by X-ray photoemission spectroscopy (XPS) are given in the Table. 3. The concentrations of Fe and Ag in the composite were negligible (0.52 and 0.18 at.%), respectively; an order of magnitude less than the concentrations of Fe and Ag established by the EDX method. The ratio of [O/Si] atoms is close to stoichiometric (2.05), which directly confirms that the main volume of the ternary composite is in SiO_{2NPles}. The low concentration of excess oxygen with a slight concentration of AgNPles leads to the loss of a number of useful properties in the ternary composite, namely: the magnetization of the composite has significantly decreased and the powders have lost buoyancy in water, unlike the Fhy-Ag double composite (Table.3), in which these useful properties were pronounced. Curiously, XPS analysis showed the absence of nitrogen atoms in the ternary composite, while from XRD data it follows that nitrogen atoms should be present in the sample, since according to XRD data, $AgNO_3$ crystals form the basis of the composite (100 wt.%).

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

Sample	Concentration, at. %						
	[O]	[Si]	[Fe]	[N]	[C]	[Ag]	[O/Si]
Fhy-SiO_2-Ag	64.28	31.38	0.52	-	3.64	0.18	2.05
Fhy [7]	40.5		11.1	5.5	42.9	-	-
Fhy-Ag	63.90	-	7.77	-	27.60	13.36	-

4. Conclusion

For the first time, using the radiation-chemical method, in a mixture of an alcohol solution of two iron and silver nitrates with an alcohol suspension of NPles Aerosil90, a synthesis of a ternary mesoporous nanocomposite "ferrihydrite-silicon oxide-silver" was carried out.

Element analysis data by XPS and EDX confirmed the presence of Ag and Fe in the composition of the composite at a low concentration, which indicates a significant inhibition of the process of formation of NPlesFh and Ag in the presence of NPles silicon in suspension. SEM

images and satisfactory texture parameters (BET Surface Area = 29.81 m^2/g, pore volume = 0.077 cm^3/g and Pore Size = 23.42 nm) confirmed the mesoporous type of the resulting composite, indicating the prospect of its use as an adsorbent in cleaning water of contaminants or nanocontainer in various biomedical applications.

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